이학석사학위논문

Long-term changes of persistent toxic substances and potential toxicities in the sediments along the west coast of Korea

서해연안 퇴적물 내 잔류성 오염물질 및 잠재적 독성의 장기변화 특성 평가

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이 논문을 이학석사 학위논문으로 제출함

2019년 4월

서울대학교 대학원

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김 선 주의 이학석사 학위논문을 인준함

2019년 6월

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Abstract

Long-term changes of persistent toxic substances and potential toxicities in the sediments along the west coast of Korea

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The west coast of Korea, including various estuarine and coastal regions, has been experienced environmental deterioration from industrialization and urbanization for decades. This study focuses on i) long-term changes of persistent toxic substances (PTSs) in these areas, ii) the sources of each pollutant by analyses of chemical compositions, iii) evaluation of potential toxicities of sedimentary pollutants using cell lines and *Vibrio fischeri* bioassay, and iv) identification of the causative chemicals through the relationships between PTS concentrations and biological responses. Sediment samples have been collected from estuarine and coastal regions from year 2010 to 2018 annually. Target PTSs include 15 polycyclic aromatic hydrocarbons (PAHs), 10 styrene oligomers (SOs), 3 nonylphenols (NPs), and 8 heavy metals (HMs). The gas chromatograph coupled with a mass selective detector (GC/MSD) was used to determine the concentration of PAHs, SOs, and NPs, while inductively coupled plasma mass spectrometry (ICP/MS) and inductively coupled plasma optical emission spectrometry (ICP/OES) was used for HMs. This study conducted bioassays to determine AhR-mediated potency, ER-mediated potency, and bioluminescence inhibition rate using H4IIE-*luc*, MVLN cell lines, and *V. fischeri*, respectively.

The trends of PTSs concentrations were generally decreased for the period between 2010 and 2018. Reduction rates of PAHs, SOs, and NPs were 63.9%, 95.0%, and 44.5%, respectively. The results suggested that the PAHs were majorly originated from pyrogenic sources including biomass or fuel combustions. After year 2015, the PAHs from vehicle emission were dominants in sediment samples. The fresh inputs of SOs were gradually decreased since 2010 and eventually, there was no fresh input found in sediments collected in 2018. The NP concentrations also decreased from year 2010 to 2018 which can be resulted from strict regulations of these NPs by the Korean government.

On the other hand, the PAH concentrations showed a positive relationship with AhR-mediated potencies ($r = 0.53$, $p < 0.01$) and so did the NP concentrations with ER-mediated potencies ($r = 0.31$, $p < 0.01$). Also, Cd concentrations showed significant correlation with bioluminescence inhibition rates of *V. fischeri* ($r = 0.47$, $p < 0.01$). Nevertheless, the result of potency balance analyses between BaP-EQ and BEQ, E2-EQ and EEQ values indicated that the target pollutants analyzed in this study had little effect on total AhR and ER-mediated potencies in sediments. These findings reflected that target PTSs in this study could not be the major pollutants having potential biological toxicities. Therefore, it would be desirable to have more studies on identifying and monitoring of the causative chemicals in sediments.

Keywords: PAHs, Nonylphenols, Styrene oligomers, Heavy metals, Bioassays, Sediments

Student Number: 2017-20790

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Abbreviations

AAS	Atomic absorption spectroscopy
Ace	Acenaphthene
Acl	Acenaphthylene
AhR	Aryl hydrocarbon receptor
Ant	Anthracene
As	Arsenic
BA	Boric acid
BaA	Benzo[*a*]anthracene
BaP	Benzo[*a*]pyrene
BbF	Benzo[*b*]fluoranthene
BghiP	Benzo[*g,h,i*]perylene
BkF	Benzo[*k*]fluoranthene
BPA	Bisphenol-A
CCME	Canadian sediment and soil quality guidelines
Cd	Cadmium
Chr	Chrysene
Cr	Chromium
Cu	Copper
DbahA	Dibenz[*a,h*]anthracene
DCM	Dichloromethane
DMSO	Dimethyl sulfoxide
E2	17β-estradiol
EPA	Environmental Protection Agency
ER	Estrogen receptor
FBS	fetal bovine serum
Fl	Fluoranthene
Flu	Fluorene
GC/MSD	Gas chromatography-mass selective detector
$HClO_4$	Perchloric acid

HF	Hydrofluoric acid
Hg	Mercury
HMs	Heavy metals
HMW	High molecular weight
HNO_3	Nitric acid
HQ	Hazard quotients
IcdP	Indeno[*1,2,3-cd*]pyrene
ICP/MS	Inductively coupled plasma mass spectrometry
ICP/OES	Inductively coupled plasma optical emission spectrometry
ISQG	interim sediment quality guidelines
LMW	Low molecular weight
MOE	Ministry of environment
N.c.	Not collected
N.d.	Not detected
Ni	Nickel
NP1EO	Nonylphenol monoethoxylates
NP2EO	Nonylphenol diethoxylate
NPs	Nonylphenols
PAHs	Polycyclic aromatic hydrocarbons
Pb	Lead
Pery	Perylene
Phe	Phenanthrene
PMF	Positive matrix factorization
POPs	Persistent organic pollutants
PTS	Persistent toxic substances
Py	Pyrene
RePs	Relative potencies
RLU	relative luminescence units

SD1	1,3-Diphenylproane
SD2	*cis*-1,2Diphenylcyclobutane
SD3	2,4-Diphenyl-1-butene
SD4	*trans*-1,2-Diphenylcyclobutane
SDs	Styrene dimers
SOs	Styrene oligomers
SQGs	Sediment quality guidelines
ST1	2,4,6-Triphenyl-1-hexene
ST2	1e-Phenyl-4e-(1-phenylethyl)-tetralin
ST3	1a-Phenyl-4e-(1-phenylethyl)-tetralin
ST4	1a-Phenyl-4a-(1-phenylethyl)-tetralin
ST5	1e-Phenyl-4a-(1-phenylethyl)-tetralin
ST6	1,3,5-Triphenylcyclohexane
STs	Styrene trimers
TCDD	2,3,7,8-tetrachlorodibenzo-*p*-dioxin
TEL	Threshold effect level
TEQs	Toxic equivalents
Zn	Zinc

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Chapter 1. Introduction

The west coast of Korea has undergone significant urbanization and industrialization for decades. These rapid changes have not only brought economic development but also have resulted in local contamination with persistent toxic pollutants (PTSs) (Khim et al., 1999; Kim et al., 2007). Several rivers including the Han River, Geum River, and Yeongsan River, discharge fresh water directly into the Yellow Sea and the exchange of sea water is relatively slow. Lot of pollutants can be released from both agricultural and chemical productions from the drainage parts of these rivers. (Hong et al., 2012a; Naile et al., 2011). As a result, PTSs tend to accumulate in the sediments and impact on benthic organisms, which could ultimately influence human beings through bioaccumulations (Christophoridis et al., 2009; Dassenakis et al., 2003).

PTSs, such as polycyclic aromatic hydrocarbons (PAHs), nonylphenols (NPs), styrene oligomers (SOs), and heavy metals (HMs) have been found in industrial and agricultural areas in the west coast (Hong et al., 2016; Koh et al., 2002, 2006). PAHs have been considered as prominent contaminants in sediments from Korean coastal areas because of their mutagenicity, carcinogenicity, and toxic effects on marine organisms (Khim and Hong, 2014; Kim et al., 1997; Koh et al., 2002). They were also known as the major aryl hydrocarbon receptor (AhR) agonists. Moreover, the US Environmental Protection Agency (EPA) listed PAHs as priority pollutants (Keith and Telliard, 1979). SOs are emerging pollutants originated from the degradation of plastics in marine environments (Kwon et al., 2014). They can cause adverse effects such as genotoxic, reproduction toxicities and disrupt the nervous system in marine organisms (Ohyama et al., 2001). NPs are degradation products of nonylphenol ethoxylates (NPEOs) and can disrupt the endocrine systems of marine organisms (Koniecko et al., 2014).

Therefore, the production and use of some nonylphenol applications have been prohibited and regulated strictly (Soares et al., 2008). On the other hand, great concentration of HMs with their stabilities, persistence, and bioaccumulation can cause sediments toxicities and have a huge impact on the marine organisms (Gao et al., 2016, 2018; Roman et al., 2007, Ryu et al., 2016). Especially, arsenic (As) is known as a carcinogenic element and exists in pesticides, fertilizers and combustion of fossil fuel. Lead (Pb) is known to exist in the exhaust gas, coal combustion, and factory wastewater, and can cause physiological and neurological disorders to human health (Aksentijević et al., 2012; Li et al., 2012; Liu et al., 2007; Nriagu, 1996). Therefore, a study of the distributions of PTSs in sediments is important to assess the influence of anthropogenic activities on the marine environments.

Instrumental analysis of pollutants in sediments can identify the concentrations of target pollutants, but there is a disadvantage of inability to determine the integrated biological potencies that the target pollutants actually induce. Even if target pollutants are not analyzed due to their low concentration below the sediment quality guidelines or even the detection limit, they may act independently or interact with agonists to influence the biological potencies of the mixture of pollutants present in the marine environments. H4IIE-*luc* and MVLN bioassays are the tools of assessing the potencies which are mediated with aryl hydrocarbon receptor (AhR) and estrogen receptor (ER), respectively (Hong et al., 2012a, 2012b; Jeon et al., 2017). N-Tox bioassay is based on the inhibition of bioluminescence of the marine bacterium *V. fischeri* following the exposure to toxicants. This method is a useful analysis to evaluate the toxicological impact of a mixture of pollutants in the marine environments (Bulich, 1986; Jacobs et al., 1993). Thus, combined use of instrumental analysis and bioassays would be a more powerful tool of assessment of sediment pollutants (Figure 1) (Khim et al., 2001b; Macikova et al., 2014).

Long-term distributions and concentrations of PTSs in the west coast of Korea have been scarcely studied. This study aims to; i) seek trends in the distributions of PTSs (15 PAHs, 10 SOs, 3 NPs, and 8 HMs) at estuarine and coastal areas along the west coast of Korea, ii) identify the sources and fresh inputs of each pollutant by analyses of chemical compositions, iii) assess the potential toxic effects of sedimentary contaminants using H4IIE-*luc*, MVLN and *V. fischeri* assays, and iv) identify the causative chemicals through the relationships between PTS concentrations and biological responses. This study provides nine-year changes of target pollutants concentrations and biological responses in the west coast, which certainly aids the current information on environmental database following future directions on their monitoring and regulations.

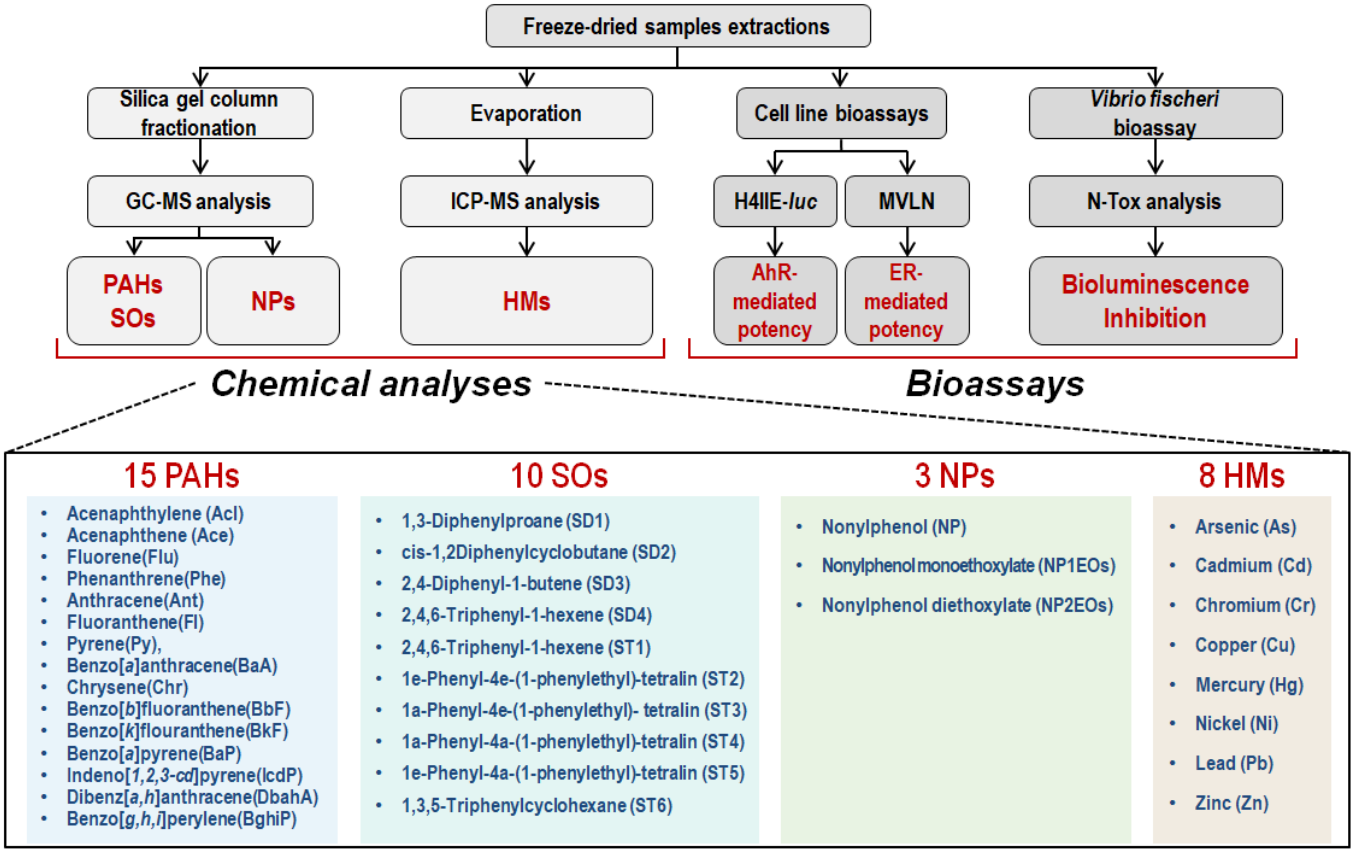


Figure 1. Flowchart of the present study**.**

Chapter 2. Materials and Methods

2.1 Sampling and sample preparation

Surface sediment samples have been annually collected from at 10 locations of estuarine and coastal areas along the west coast of Korea for 9 years from year 2010 to 2018 (Naile et al., 2010). LS and YS are areas where large industrial complexes have been developed since 1987 and 1994, respectively. AS, SG, and GG sites have developed agricultural complexes nearby. In addition, tourism complexes have been built near the AS and SG, and commercial facilities have been developed since 1994. There is a bird ecological exhibition hall near GG peak and also, there is a discharge water drain close the GG. As a result of reviewing the PTS concentrations in the sediments from the west coast from the 1990s to the 2010s, the concentrations were lower than the sediment quality guideline since 2000s in most sites (Figure 2). In this study, sites were selected to compare the concentrations of PTSs in the sediments of the inner and outer sides of the sea dikes. Table 1 and Figure 3 present the sampling information and the maps of 10 sampling sites. The construction period of the sea dike for each sites is LS in 1994, AS in 1973, SG in 1979, GG in 1989 and YS in 1981. The inner and outer regions of sea dikes were marked as “1” and “2”, respectively (Figure 3). All samples were transported immediately to the laboratory and stored at -20 ℃ until analysis. All samples were freeze-dried and ground before analysis. Detailed descriptions of sample preparation for PTSs and in vitro analysis have been published previously (Hong et al., 2012a, 2015). 20 g of each sample was extracted for 16 h on a Soxhlet extractor with 350 mL dichloromethane (DCM, Burdick & Jackson, Muskegon, MI). Elemental sulfur was removed by adding activated copper powder (Sigma-Aldrich, Saint Louis, MO). The extracts were concentrated to 2 mL and separated into two aliquots for use in the instrumental analysis and the *in vitro* bioassays.

For chemical analyses, 1 mL of the aliquot was passed through 8 g of activated silica gel (70 - 230 mesh, Sigma-Aldrich) column for fractionation into two fractions (F1: aromatics; F2: polar). The fractions were eluted with 50 mL of 20% DCM in hexane (F1) and 50 mL of 60% DCM in acetone (F2), respectively. Prior to instrumental analysis, elutriates were concentrated to 1 mL by rotary evaporator, followed by gentle nitrogen gas. For the *in vitro* bioassay, the aliquot was exchanged into dimethyl sulfoxide (DMSO, Sigma-Aldrich).

The HM analyses and bioluminescence test by *V. fischeri* were based on the standard method of Korea's Ministry of Oceans and Fisheries (MOF, 2018) with some modifications. For the HMs analyses except As and Hg, 0.2 g of samples was digested in Teflon beaker with 3 mL of HNO_3 and 1 mL of $HClO_4$ for 4 h. After evaporated near dryness, 3 mL of HF and 1 mL of $HClO_4$ were added and heated at 140 ℃ for 6 h. Then, the same procedure was repeated one more time. After cooling to room temperature, the samples were evaporated with 2 mL of $HClO_4$ and 5 mL of BA. After diluted with 1% HNO_3, the extracts were concentrated to 10 mL. For the determination of As, 0.2 g of samples was digested with 10 mL of 10% HNO_3 for 24 h and then centrifuged at 2000 × g at 25 ℃ for 10 min. For Hg, 0.5 g of samples was digested with 50 mL of 10% HCl for 24 h and then centrifuged at 2000 × g at 25 ℃ for 10 min. Each supernatant was collected for instrumental analysis. For the bioluminescence analysis, 2 g of samples was placed in a 50 mL Teflon™ centrifuge tube. The samples were extracted with 20 mL filtered seawater by mechanical shaking at 200 rpm for 1 h. After centrifuged for 3 min. at 2000 rpm, the supernatant was filtered through 1.0 μm membrane filter for further analysis.

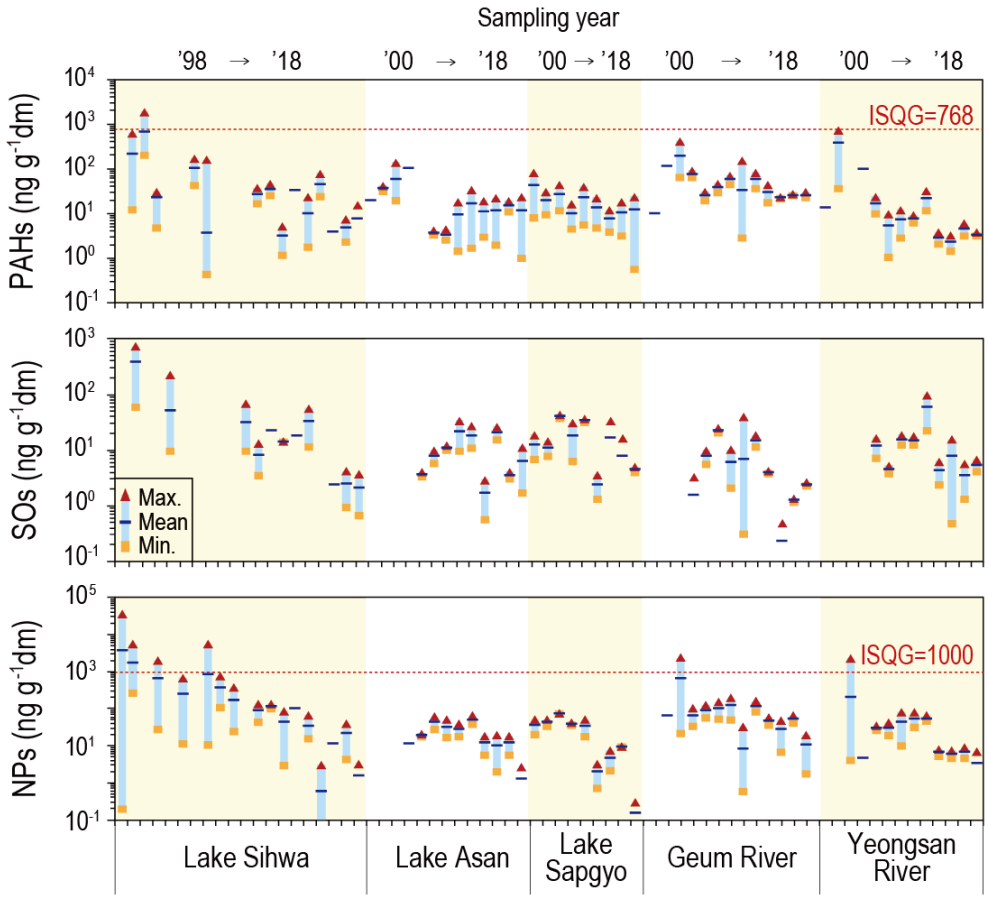


Figure 2. Summary of concentrations and distributions of PAHs, SOs, and NPs in sediments along the west coast from 1990s to 2018.

Table 1. Sampling year and geological description of sampling sites.

Sampling					**Remark**
Area	**Location**	**Station**	**Year**	**n**	**Geological description**
Gyeonggi	Lake Sihwa	LS1	2010, 2012, 2014, 2017, and 2018	5	Inside of sea dike
		LS2	2010 to 2018	9	Coastal area, outside of sea dike
Chungnam	Lake Asan	AS1	2010 to 2018	9	Inside of sea dike
		AS2	2010 to 2018	9	Coastal area, outside of sea dike
	Lake Sapgyo	SG1	2010 to 2018	9	Inside of sea dike
		SG2	2010 to 2018	9	Coastal area, outside of sea dike
Jeonbuk	Geum River	GG1	2010 to 2018	9	River, inside of sea dike
		GG2	2010 to 2018	9	Coastal area, outside of sea dike
Jeonnam	Yeongsan River	YS1	2010 to 2018	9	River, inside of sea dike
		YS2	2010 to 2018	9	Coastal area, outside of sea dike

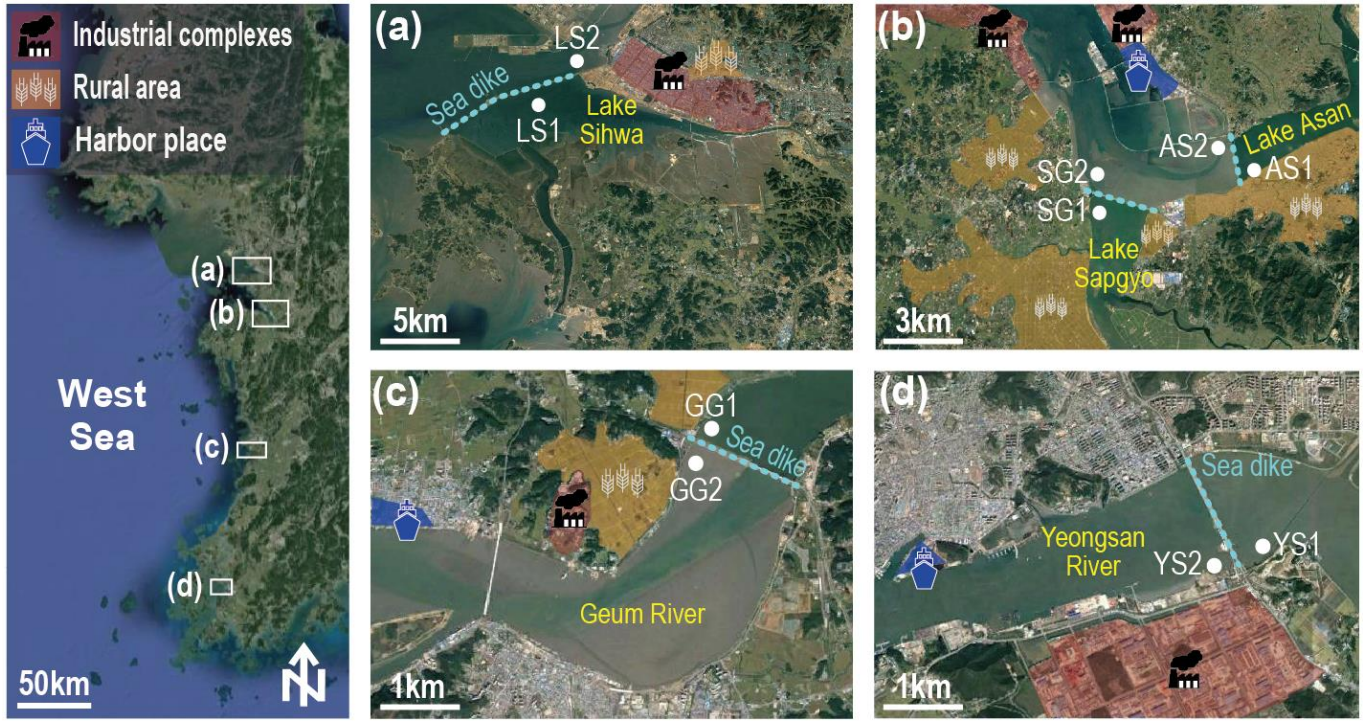


Figure 3. Maps showing the study areas. (a) Lake Sihwa, (b) Lake Asan and Sapgyo, (c) Geum River, and (d) Yeongsan River. In the symbol of each sampling site, the number "1(2)" represents the inner (outer) region of sea dike.

2.2 Chemical analyses

Concentrations of PAHs, SOs, and NPs in the sediment extracts were identified and quantified by using a GC/MS (MSD, Agilent Technologies, Santa Clara, CA). Details of instrument setting and PTSs were provided in Table 2. A total 15 PAHs, 10 SOs, 3 NPs were analyzed according to the method previously reported (Jeon et al., 2017). The detection limits of 15 PAHs, 10 SOs, 3 NPs were 0.16 to 0.56 ng g^{-1} dry mass (dm), 0.23 to 4.20 ng g^{-1} dm, and 0.45 to 0.70 ng g^{-1} dm, respectively. Concentrations of 15 PAHs and 3 NPs in the sediment samples from 2010 to 2014 were cited from previous study (Jeon et al., 2017). HMs in the sediment extracts were quantified by use of inductively coupled plasma mass spectrometry (ICP/MS; ELAN 6100 System, PerkinElmer, Waltham, MA) and inductively coupled plasma optical emission spectrometry (ICP/OES; Optima7300DV, PerkinElmer) except Hg. Hg were quantified by using Atomic absorption spectroscopy (AAS; Fims100, PerkinElmer). HMs pollutions were expressed in sum of hazard quotients (ΣHQ_{metals}) (Equation (1)) (Ryu et al., 2016).

$$\Sigma HQ_{metals} = \Sigma C_{metal}/C_{reference} \quad \text{(Eq. 1)}$$

Where, C_{metal} is the HMs concentrations in the sediment samples and $C_{reference}$ is the concentrations of sediment quality guideline (Cr: 116 mg kg^{-1}; Cu: 20.6 mg kg^{-1}; Pb: 44.0 mg kg^{-1}; Ni: 47.2 mg kg^{-1}; As: 14.5 mg kg^{-1}; Hg: 0.11 mg kg^{-1}; Zn: 68.4 mg kg^{-1}; Cd: 0.75 mg kg^{-1} for Korean Threshold Effects Level (TEL)) (MOF, 2013). The ΣHQ_{metals} value was calculated by combining factors ($C_{metal}/C_{reference} > 1$) for HMs in sediments.

Table 2. GC/MSD instrument conditions for determination of 15 PAHs, 10 SOs, and 3 NPs.

GC/MSD system	**Agilent 7890A GC and 5975C MSD**	
Column	DB-5MS (30 m long × 0.25 mm i.d × 0.25 μm film thickness)	
Gas flow	1.0 mL $min.^{-1}$ (He)	
MS temperature	180 ℃	
Detector temperature	230 ℃	
Oven temperature	60 ℃ hold 2 min. Increase 6 ℃ $min.^{-1}$ to 300 ℃ 300 ℃ hold 13 min.	60 ℃ hold 5 min. Increase 10 ℃ $min.^{-1}$ to 100 ℃ Increase 20 ℃ $min.^{-1}$ to 300 ℃ 300 ℃ hold 6 min.
Injection volume	2 μL	1 μL
Target Compounds	Acenaphthylene (Acl), Acenaphthene (Ace), Fluorene (Flu), Phenanthrene (Phe), Anthracene (Ant), Fluoranthene (Fl), Pyrene(Py), Benzo[*a*]anthracene (BaA), Chrysene (Chr), Benzo[*b*]fluoranthene (BbF), Benzo[*k*]fluoranthene (BkF), Benzo[*a*]pyrene (BaP), Perylene (Pery), Indeno[*1,2,3-cd*]pyrene (IcdP), Dibenz[*a,h*]anthracene(DbahA), Benzo[*g,h,i*]perylene (BghiP), 1,3-Diphenylproane (SD1), cis-1,2Diphenylcyclobutane (SD2), 2,4-Diphenyl-1-butene (SD3), 2,4,6-Triphenyl-1-hexene (SD4), 2,4,6-Triphenyl-1-hexene (ST1), 1e-Phenyl-4e-(1-phenylethyl)-tetralin (ST2), 1a-Phenyl-4e-(1-phenylethyl)-tetralin (ST3), 1a-Phenyl-4a-(1-phenylethyl)-tetralin (ST4), 1e-Phenyl-4a-(1-phenylethyl)-tetralin (ST5), and 1,3,5-Triphenylcyclohexane (ST6)	Nonylphenol (NP), Nonylphenol monoethoxylate (NP1EO), and Nonylphenol diethoxylate (NP2EO)

2.3 Bioassays

The H4IIE-*luc* and MVLN bioassays were performed to measure the AhR and ER-mediated potencies in the sediment extracts, respectively, according to previously published methods (Khimet al., 1999; Hong et al., 2012). The H4IIE-*luc* cells were incubated in Dulbecco's modified eagle's medium-low glucose (DMEM, Sigma-Aldrich) with 10% fetal bovine serum (FBS, Sigma-Aldrich) in CO_2 incubator at 37 ℃. The MVLN cells were incubated in Dulbecco's modified eagle's medium/Nutrient mixture F-12 Ham (DMEM/Ham, Sigma-Aldrich) with 10% FBS (Sigma-Aldrich) in CO_2 incubator at 37℃. H4IIE-*luc* bioassay responses were expressed as the mean relative luminescence units (RLU). Then the RLU converted to percentages of the maximum response of 50 nM benzo[*a*]pyrene (BaP) (%BaP_{max}). Responses of the MVLN bioassay were converted to RLU by percentage of the maximum response of 1235 nM 17β-estradiol (E2) (%$E2_{max}$). Trypsinized H4IIE-*luc* and MVLN cells were diluted to a concentration of approximately 7×10^4 cell mL^{-1} and 1.25×10^5 cell mL^{-1}, respectively and seeded into the 96-well plate (Perkin Elmer, MA, USA) with 250 mL of medium per well. After incubation for 24 h, the cells were exposed to sediment extracts dosed at 0.25 mL (0.1% dose) with each cell's durations of exposure (4 h and 72 h). After exposure, the luminescence of luciferase was quantified by using a Victor X3 multi label plate reader (Perkin-Elmer). Significant level was defined as three times the standard deviation of the mean of the solvent controls and expressed in %standard max (Horii et al., 2009). AhR and ER-mediated potencies from year 2010 to 2014 were cited from previous study (Jeon et al., 2017).

Table 3. Description and culture conditions of recombinant cells using bioassay.

Name	**H4IIE-*luc***	**MVLN**
Organism	Rat *(Rattus norvegicus)*	Human *(Homo sapiens)*
Tissue	Liver	Mammary gland/breast
Cell type	Recombinant (Luc)	Recombinant (Luc)
Culture condition	37 ℃, 5% CO_2	37 ℃, 5% CO_2
Culture properties	Adherent	Adherent
Disease	Hepatoma	Adenocarcinoma
Exposure time	4 h	72 h
End-point	AhR binding affinity (dioxin-like activity)	ER binding affinity (estrogenic activity)
Positive control	BaP	E2
Agonists	PAHs, PCDD/Fs, etc.	NPs, OPs, BPA, etc.
Measurement	Luciferase assay	Luciferase assay

The *V. fischeri* bioluminescence bioassay was conducted with a luminescent bacteria toxicity measurement instrument (N-TOX model 200; NeoEnBiz Inc., Bucheon, Korea) according to method of the Ministry of Maritime Affairs and Fisheries of South Korea (MOMAF, 2005) with some modifications. Detailed descriptions of sediment sample preparation procedures for the bioluminescence assay have been reported previously (Lee et al., 2008). 1 mL reconstituted solution of VF100® (NeoEnBiz Inc.) was added to the lyophilized *V. fischeri* to reactivate *V. fischeri*. A bacterial solution consisted of 1 mL of bacterial reagent with 50 mL of diluent (at 4 ℃). The suitable reactivation time is about 20 - 30 min. for *V. fischeri*. Before the test a zinc sulfate solution was pretested as a reference chemical compared with every fresh bacteria to ensure effectiveness in all tests (ISO, The International Organization for Standardization, 1998). Serially-diluted test water and sediment extracts were prepared into a 96-well plate (250 μL to each well). Then, 25 μL of bacterial solution was added to each well. Luminescence was measured at 10 min. intervals for a total of 30 min. to track changes in light intensity. The determination of potential toxicity by *V. fischeri* bioluminescence test was performed following 30 min. contact in all sediment extracts.

Table 4. Description of test conditions and test acceptability criteria for luminescent bacteria test.

Parameters	**Test conditions**
Test type	Luminescent bacteria test for liquid phase sample
Sample type	Fresh water, salt water, pore water, ground water, any other aqueous liquid phase samples
Test species	Freeze-dried *Vibrio fischeri*; NRRL B-11177 (N-Tox VF100)
Diluent	DW100 for fresh water / DW200 for salt water
Test chamber	96-well plate
Test volume	250 µl (max)
Temperature	15 ℃
Test duration	30 min.
Instrument	N-Tox Model 200
Endpoint	Inhibitory effect after 30 min. exposure
Test acceptability criteria	1) Variation of natural light emission rate between 0 and 30 min. must be 0.6 - 1.8 2) The following reference toxicants cause 20% - 80% inhibition by 30 min. exposure (a) 3.4 mg L^{-1} of 3,5-dichlorophenol (b) 2.2 mg L^{-1} of Zn^{2+} (as zinc sulfate heptahydrate) (c) 18.7 mg L^{-1} of Cr^{6+} (as potassium dichromate)

2.4 Potency balance analyses

Potency balance analyses between instrument-derived BaP equivalent concentrations (BEQs) and bioassay-derived concentrations in sediments were conducted to evaluate the relative contribution of each target pollutants to the total induced AhR and ER-mediated potency. AhR-mediated potencies were expressed as BaP equivalent concentrations (pg BaP-EQ g^{-1} dm) and ER-mediated potencies were expressed as E2 standard equivalent concentrations (pg E2-EQ g^{-1} dm). These concentrations were determined directly from the sample dose-response relationships generated by testing samples at multiple levels of dilution (Louiz et al., 2008).

RePs were determined directly from the sample dose response relationships for each sample and standard curve generated from the range of standard materials (BaP and E2) dilutions. ReP50s were determined at dilutions of samples for which responses were equivalent to 50% response levels of maximum concentrations of BaP or E2 on standard curves, respectively (Hong et al., 2012a; Lee et al., 2017). BEQ were calculated with ReP values of each PAHs compound (Acl, Flu, Py, BaA, Chr, BbF, BkF, BaP, IcdP, and DbahA) and EEQ were calculated with those of NPs (NP, NP1EO, and NP2EO) (Villeneuve et al., 1998). All samples were performed in triplicates.

2.5 Data analyses

Spearman correlation analysis was conducted using SPSS 23.0 (SPS INC., Chicago, IL) to determine the relationship between HMs concentrations and *V. fischeri* bioluminescent inhibition rates in sediment samples. The positive matrix factorization (PMF) receptor model developed by Paatero and Tapper (1994) and Paatero (2000), is a multivariate factor analysis approach for quantifying the contribution of sources to samples based on the composition or fingerprints of the sources (Nicolás et al., 2008). PMF is a useful factorization method that can calculate source profile and contribution (Zhang et al., 2012). A dataset was analyzed by use of the US EPA PMF 5.0 model to estimate the source contributions to Σ 15 PAHs in sediments. The model was downloaded from the homepages of US-EPA (http://www.epa.gov).

Chapter 3. Results and Discussion

3.1 Spatio-temporal distributions of persistent toxic substances

3.1.1 Polycyclic aromatic hydrocarbons

Concentrations of 15 PAHs in sediments were ranged from 0.0 to 93.5 ng g^{-1} dm (mean: 19.0 ng g^{-1} dm) in all samples. The detection limits of each PAHs compound ranged from 0.16 to 0.56 ng g^{-1} dm. In some sampling sites (LS1 and YS1 collected from year 2018 and 2016, respectively) 15 PAHs were below the detection limits. From 2010 to 2018, annual distributions of 15 PAHs showed a slightly decreasing trend (Figure 4). The annual mean concentrations of 15 PAHs were 34.5 ng g^{-1} dm in 2010, 22.6 ng g^{-1} dm in 2011, 16.4 ng g^{-1} dm in 2012, 23.3 ng g^{-1} dm in 2013, 27.8 ng g^{-1} dm in 2014, 13.4 ng g^{-1} dm in 2015, 10.9 ng g^{-1} dm in 2016, 12.3 ng g^{-1} dm in 2017, and 12.4 ng g^{-1} dm in 2018, respectively. This could be explained by effects of regulations on persistent organic pollutants by Ministry of Environment (MOE, 2008). In order to regulate the production and use of persistent organic pollutants (POPs), the Ministry of Environment collects POPs from all over the country every year.

The mean concentrations of 15 PAHs in each site were 13.0 ng g^{-1} dm at LS1, 12.0 ng g^{-1} dm at LS2, 6.3 ng g^{-1} dm at AS1, 20.5 ng g^{-1} dm at AS2, 5.4 ng g^{-1} dm at SG1, 31.5 ng g^{-1} dm at SG2, 34.4 ng g^{-1} dm at GG1, 48.0 ng g^{-1} dm at GG2, 7.7 ng g^{-1} dm at YS1, and 8.0 ng g^{-1} dm at YS2. The greatest concentrations were found at GG2 followed by GG1 (Figure 5). Because of commercial facilities near GG2 and wastewater outfall near GG1, 15 PAHs could be directly introduced from those

regions. Concentrations of 15 PAHs analyzed in this study were comparable to those published in our previous study in 2008 (30 to 210 ng g^{-1} dm) (Hong et al., 2012a). Concentrations of PAHs were lower than those analyzed in other regions from the south coast of Korea (Khim and Hong, 2014). The mean concentrations were greater on the outer regions than those on the inner regions, which were likely due to the effects of salinity. Increased salinity reduces the solubility of PAHs, with a decrease of the dissolved PAHs as a result (Fernandes et al., 1997). Therefore, the probability of adsorption of PAHs to sediments would have increased in the outer regions.

High molecular weight PAHs with 4 - 6 rings of PAHs in sediment were the main compound. BkF were found to account for 45% of the total PAHs concentrations. DbahA were found to be followed at 23% of the total PAHs concentrations. These results indicated that the greater the PAHs molecular weight, the lower the acceptability and the greater the absorbency of the PAHs to the particulate matter (Choi et al., 2011).

The concentrations of 15 PAHs in all sediments samples were lower than interim sediment quality guidelines (ISQGs) recommended by CCME (Canadian sediment and soil quality guidelines (CCME), 1999). PAHs concentration in sediments from west coast reported in Lake Sihwa, Gyeonggi Bay, Taean, and Saemangeum from other studies showed relatively greater than measured in this study. Especially PAHs concentrations in inner region of sea dike in Saemangeum were 440 ng g^{-1} dm in year 1998 (Co et al., 2003). In east coast of Korea, the PAHs concentrations in Yeongil Bay and Ulsan Bay were 1800 ng g^{-1} and 1100 ng g^{-1}, respectively. (Koh et al., 2004; Moon and Kim, 2001). The areas with great PAHs concentrations were mainly in petroleum, chemical, and steel mills industrial complexes.

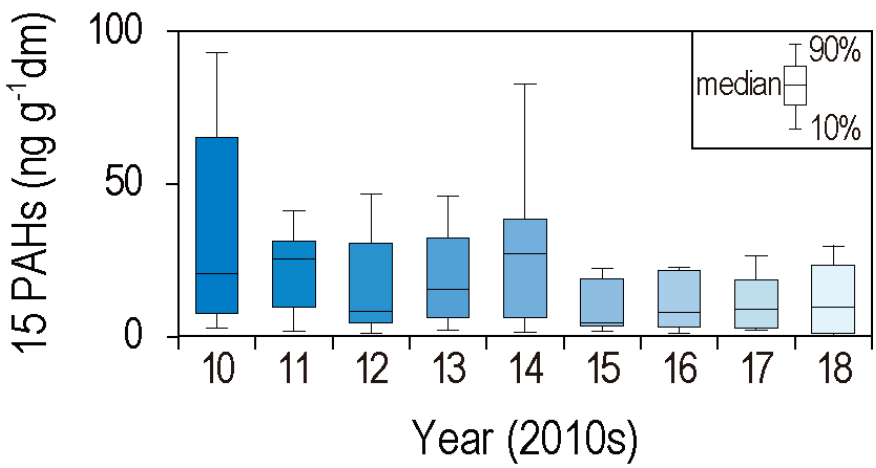


Figure 4. Annual variations of PAHs in sediments during 2010 to 2018.

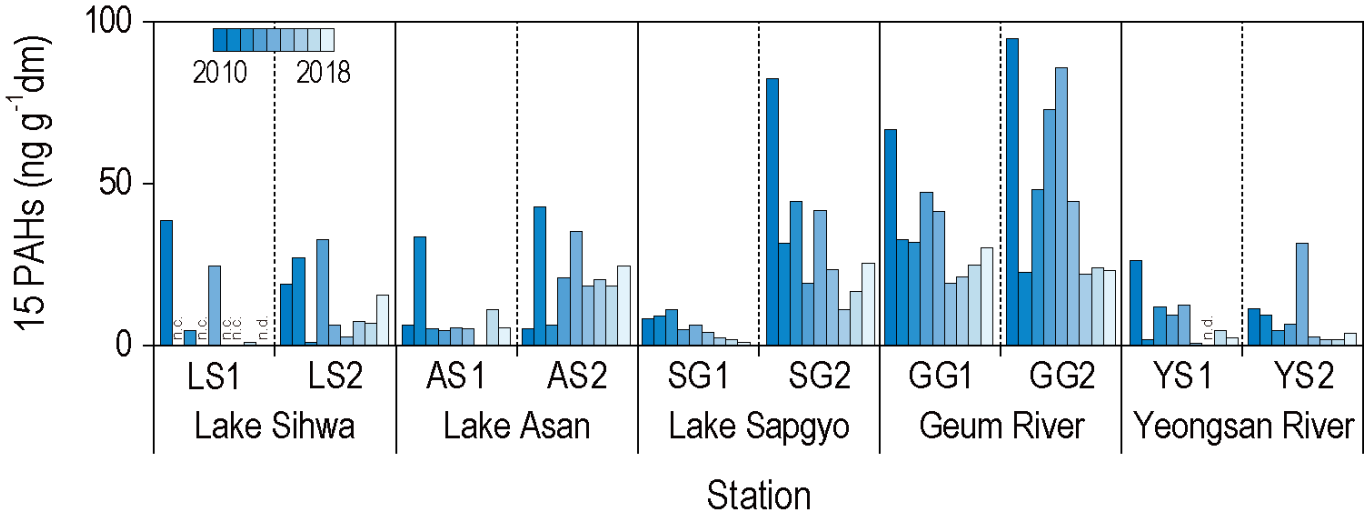


Figure 5. Spatio-temporal distributions of PAHs in sediments during 2010 to 2018.

3.1.2 Styrene oligomers

SOs are emerging pollutants derived from decomposition of polystyrene polymers from plastics in marine environments. The concentrations of 10 SOs in sediments from the west coast of Korea tend to decrease after 2014 (Figure 6). The annual mean concentrations of 10 SOs were 7.9 ng g^{-1} dm in 2010, 9.8 ng g^{-1} dm in 2011, 21.4 ng g^{-1} dm in 2012, 16.3 ng g^{-1} dm in 2013, 33.3 ng g^{-1} dm in 2014, 3.2 ng g^{-1} dm in 2015, 19.4 ng g^{-1} dm in 2016, 3.9 ng g^{-1} dm in 2017, and 4.4 ng g^{-1} dm in 2018, respectively. The detection limits of each SOs compound ranged from 0.23 to 2.20 ng g^{-1} dm. ST6 were below the detection limits in all sites.

The mean concentrations of 10 SOs in each site were 9.0 ng g^{-1} dm at LS1, 23.2 ng g^{-1} dm at LS2, 7.2 ng g^{-1} dm at AS1, 14.7 ng g^{-1} dm at AS2, 6.9 ng g^{-1} dm at SG1, 12.4 ng g^{-1} dm at SG2, 14.5 ng g^{-1} dm at GG1, 14.1 ng g^{-1} dm at GG2, 11.8 ng g^{-1} dm at YS1, and 17.4 ng g^{-1} dm at YS2. The greatest concentration of 10 SOs was found at LS2, followed by YS2 (Figure 7). The LS region is known as hot spot area contaminated by anthropogenic activities and the YS region is also near the industrial complexes surrounded by anthropogenic activities (Khim et al., 1999; Lee et al., 2017). However, since there is no sediment quality guideline for SOs yet, the 10 SOs concentrations in this study were compared with those of previously reported. Concentrations of 10 SOs in the previous studies were reported in the Lake Sihwa (10.1 to 740.0, mean 227.0 ng g^{-1} dm) in 1998, (10.1 to 70.2, mean 33.5 ng g^{-1} dm) in 2015, in the industrial areas near the Lake Sihwa (61 to 742, mean 396 ng g^{-1} dm) in 2015, in the Geum River (0.3 to 40.3, mean 7.2 ng g^{-1} dm) in 2014, in the Saemangeum (0.4 to 261.3, mean 22.0 ng g^{-1} dm) in 2014 (Hong et al., 2016; Lee et al., 2017a; Yoon et al., 2017).

The concentrations of 10 SOs analyzed in this study were similar to those of previously reported, but lower than analyzed near industrial areas. Compared with the concentrations of 10 SOs in Lake Sihwa collected in 1998, the concentrations in 2018 was decreased by 10 times (Lee et al., 2017). The distributions of the 10 SOs mean concentrations in the inner and outer regions were not significantly different. This result reflected that distributions of SOs concentration were not affected by salinity and direct or indirect inputs of SOs at all sampling sites in the west coast of Korea.

Since there is no sediment quality guideline for SOs concentrations yet, the present study provides useful information about long term concentrations and distributions of SOs in sediments from west coast of Korea as baseline data for the future study of plastic pollution. The concentrations of SOs analyzed in this study could be indicator of chemical pollution from plastics in coastal environments.

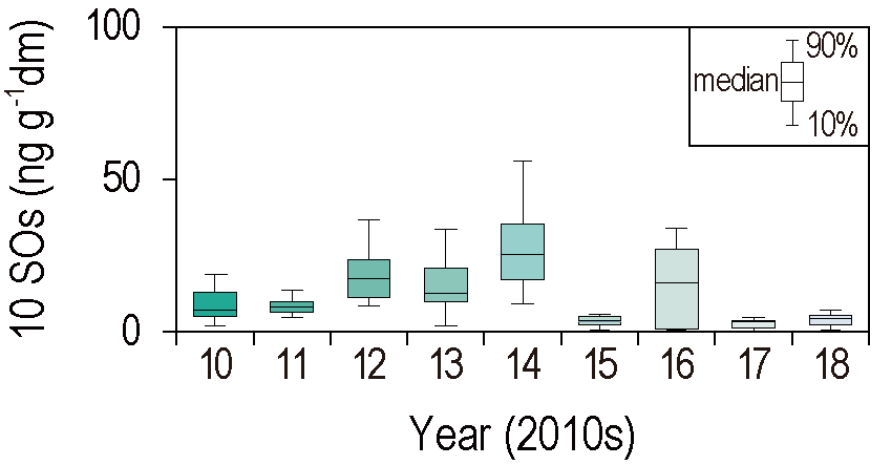


Figure 6. Annual variations of SOs in sediments during 2010 to 2018.

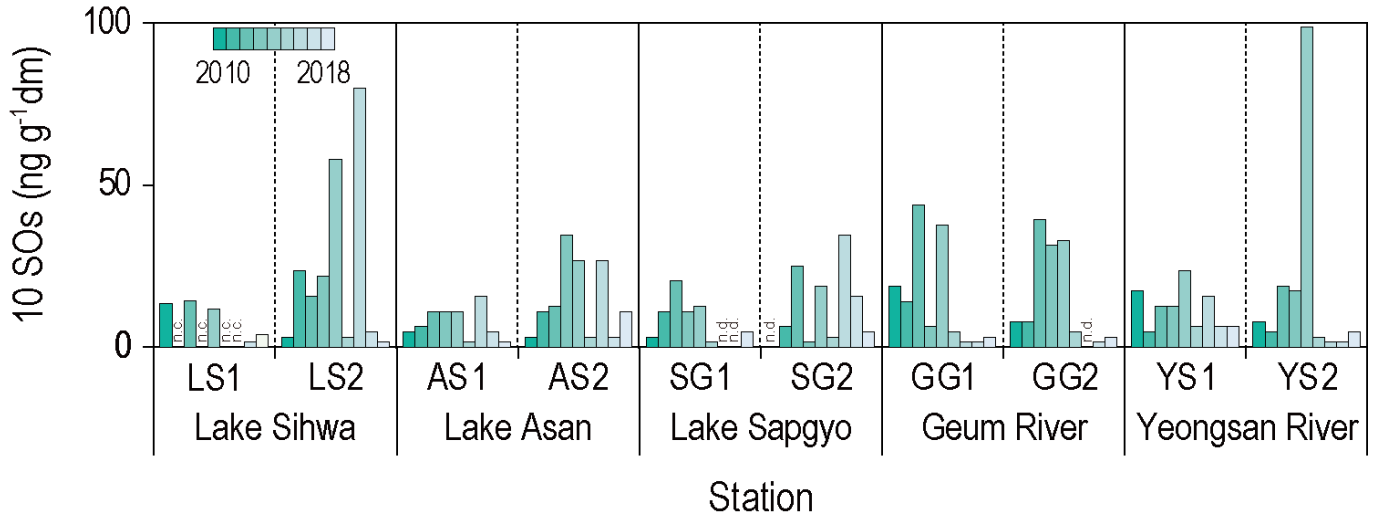


Figure 7. Spatio-temporal distributions of SOs in sediments during 2010 to 2018.

3.1.3 Nonylphenols

The concentrations of 3 NPs in sediments showed significant annual differences. The annual mean concentrations of 3 NPs were 44.1 ng g^{-1} dm in 2010, 54.2 ng g^{-1} dm in 2011, 53.8 ng g^{-1} dm in 2012, 60.5 ng g^{-1} dm in 2013, 56.0 ng g^{-1} dm in 2014, 2.9 ng g^{-1} dm in 2015, 12.2 ng g^{-1} dm in 2016, 16.7 ng g^{-1} dm in 2017, and 2.2 ng g^{-1} dm in 2018, respectively. The detection limits of each NPs compound ranged from 0.45 to 0.70 ng g^{-1} dm. Annual concentrations of 3 NPs tended to decrease after 2013 (60.5 ng g^{-1} dm) (Figure 8). This could be explained by effects of Korean government regulations on NPs applications using. The South Korean government has banned the use of NP in household cleaners in 2002, all domestic applications in 2007, paint and ink used for industrial applications in 2010 and all industrial applications in 2016 (Choi et al., 2011; Jeon et al., 2017).

The mean concentrations of 10 SOs in each site were 13.8 ng g^{-1} dm at LS1, 56.8 ng g^{-1} dm at LS2, 23.8 ng g^{-1} dm at AS1, 17.8 ng g^{-1} dm at AS2, 20.4 ng g^{-1} dm at SG1, 27.6 ng g^{-1} dm at SG2, 68.3 ng g^{-1} dm at GG1, 51.0 ng g^{-1} dm at GG2, 20.1 ng g^{-1} dm at YS1, and 28.2 ng g^{-1} dm at YS2. The greatest mean concentrations of 3 NPs were found at GG1 (68.3 ng g^{-1} dm) followed by LS2 (56.8 ng g^{-1} dm) (Figure 9.). Unlike concentrations of 15 PAHs, the mean concentrations of 3 NPs are greater in the inner regions than the outer regions of GG. These findings mean that 3 NPs could be directly discharged from the terrestrial sources like wastewater outfall near the inner regions of GG. Also, both GG and LS are hot spots of contaminants because of their industrial and municipal activities. Therefore, the mean concentrations of 3 NPs might be relatively greater at LS and GG than other sites. Similar concentration levels were shown at most sites, except for LS2, GG1, and GG2. This suggests that there is a continued inputs of NPs at every sites in sediments from the west coast of Korea. Despite the strict regulations, 3 NPs are still distributed in sediments because of their persistence characteristics. The distributions of the mean concentrations of

3 NPs had no differences between the inner and outer regions. These results revealed that 3 NPs from the surrounding areas keep contaminating the sampling sites.

NPs concentrations have been analyzed in the other studies from Lake Sihwa, Gyeonggi Bay, Gunsan, and Mokpo. The NPs concentrations reported in the inner regions of Lake Sihwa in 2000 were 3600 ng g^{-1} dm (Li et al., 2004a) and 1600 ng^{-1} gm dm (Koh et al., 2005), showing a relatively greater concentrations compared to PAHs concentrations. Because the water gates of Lake Sihwa were not opened in 2000, pollutants released into the Lake Sihwa could not be circulated and accumulated into the sediments (Koh et al., 2005). The current reduction of NP concentrations in Lake Sihwa is attributed to the exchange of seawater. Overall, the areas where showed great NPs concentrations were near the ports, petroleum and chemical complexes, and industrial complexes. There are regulations on NPs, but distributions of NPs still need to be continuously regulated and monitored as NPs were measured in sediments from the west coast of Korea.

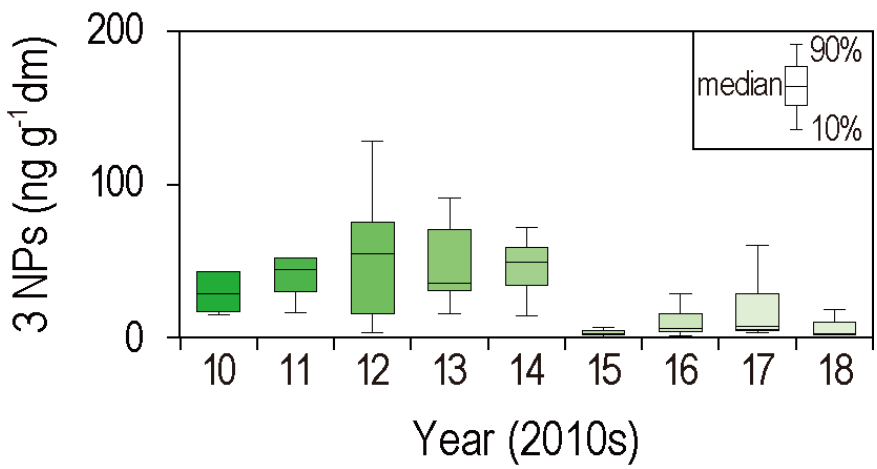


Figure 8. Annual variations of NPs in sediments during 2010 to 2018.

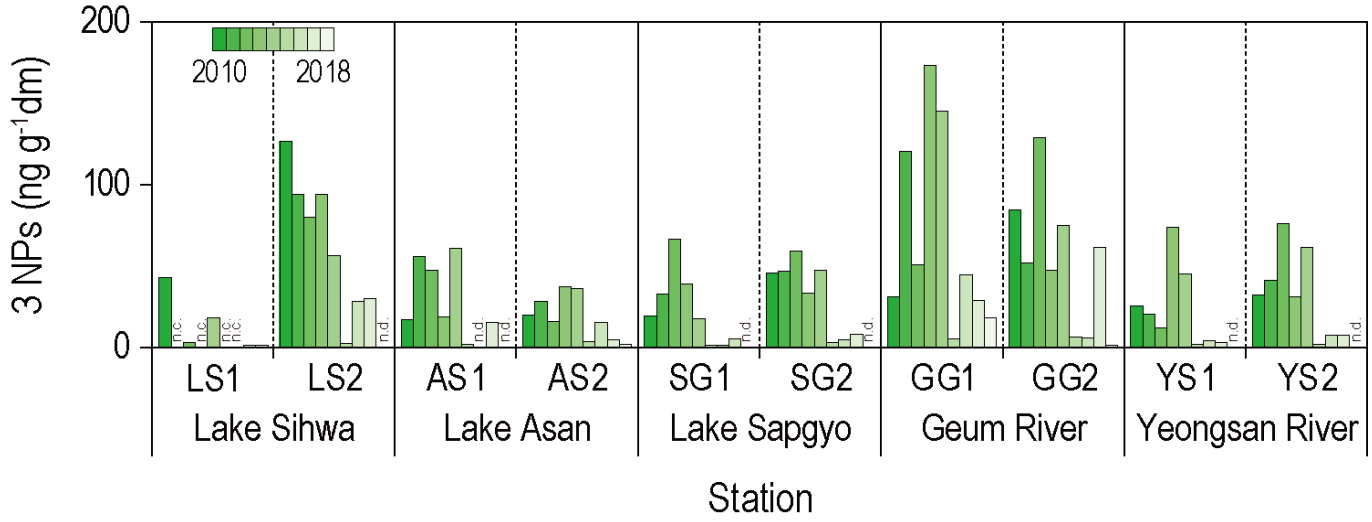


Figure 9. Spatio-temporal distributions of NPs in sediments during 2010 to 2018.

3.1.4 Heavy metals

Total 8 heavy metals (chromium (Cr), copper (Cu), lead (Pb), nickel (Ni), arsenic (As), mercury (Hg), zinc (Zn), cadmium (Cd)) were analyzed in sediment samples from the west coast of Korea. The total concentrations of HMs in sediments ranged from 42.2 to 96.5 mg kg^{-1} for Cr, 7.6 to 16.7 mg kg^{-1} for Cu, 17.9 to 36.5 mg kg^{-1} for Pb, 15.9 to 42.8 mg kg^{-1} for Ni, 3.4 to 5.8 mg kg^{-1} for As, 3.9 to 35.9 μg kg^{-1} for Hg, 40.4 to 70.6 mg kg^{-1} for Zn, and 0.1 to 0.2 mg kg^{-1} for Cd. HMs are characterized accumulation, abundance, persistence and potential toxicity in the aquatic habitats (Ali et al., 2015; Ke et al., 2017; Varol, 2011; Zhang et al., 2018). The annual ΣHQ_{metals} value were close to zero except 2010 and 2012 (Figure 10). This result indicated that the average concentrations of all HMs were lower than TEL values except 2010 and 2012. Moreover, ΣHQ_{metals} value showed distributions less than 8 in all sediment samples (Figure 11).

This means that there were no sites with all concentrations of HMs exceeding the TEL values. In addition, the concentrations of HMs in sediments of the coastal continental shelf of the world were used as the background concentration levels (Taylor, 1964). The concentrations of Cu and Cd in all sediment samples were lower than those of both background levels and TEL values (MOF, 2013). The concentrations of Hg were lower than those of both background levels and TEL in all sediment samples (Figure 12) (MOF, 2013). This indicated that the pollution of Cu, Cd, and Hg in sediments of the west coast appeared not severe.

The concentration of Cr and Ni in GG, where the concentrations of other PTSs were relatively great, partially exceeded the TEL values. There were no differences of mean concentrations of HMs between inner and outer regions of all sampling sites (Figure 12). These results mean that the salinity of sediments have not played a crucial role in the distributions of HMs. Because of their accumulation and stabilities,

HMs could potential toxic pollutants to marine organisms. It is necessary to keep investigating the distributions of HMs in sediments from the west coast Korea.

Previous studies have suggested the optimal number of study areas for the PTSs concentrations in the sediments from the Geum River (Noh et al., 2018). This study suggested that the minimum number of the study area for monitoring PTSs in the sediments is around 10 and those of HMs is around 12. For more accurate and precise monitoring, it is necessary to increase the study areas for future monitoring.

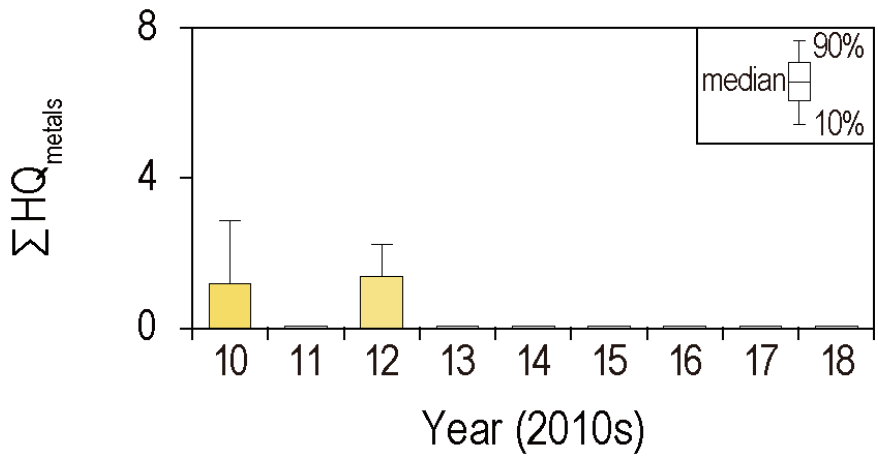


Figure 10. Annual variations of sum of HQ_{metals} values in sediments.

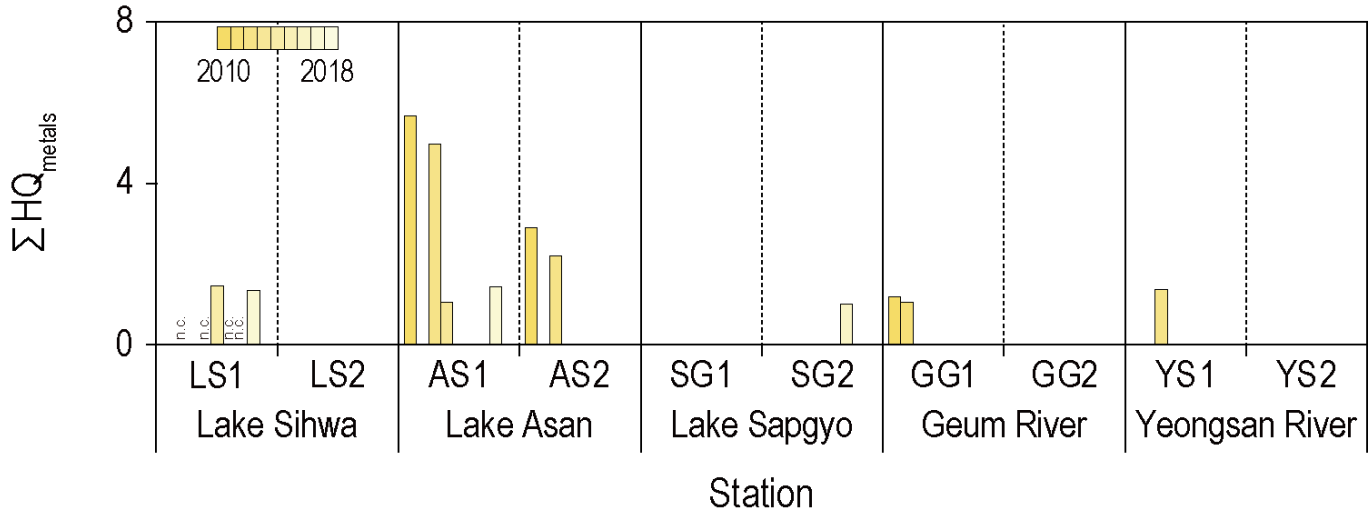


Figure 11. Regional variations of sum of HQ_{metals} values in sediments.

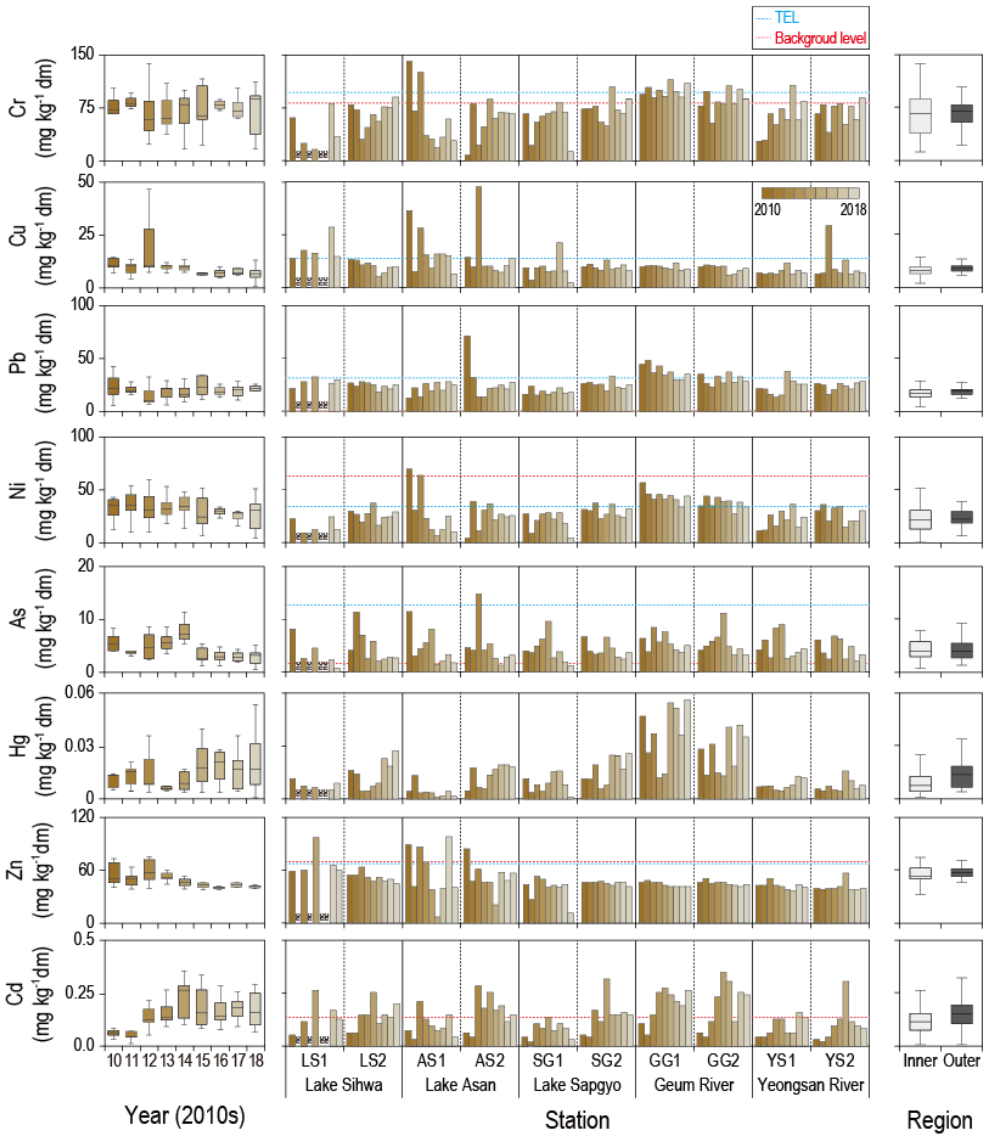


Figure 12. Spatio-temporal distributions of HMs in sediments during 2010 to 2018.

3.2 Identification of the sources and composition of PTSs

The PMF analysis was used to identify the source contributions to 15 PAHs of four factors (Figure 13) (Li et al., 2019; Zhang et al., 2012). The first factor had high concentrations for the PAH species including Ant, Acl, Py, and Fl. Ant is an important indicator of biomass combustion and Py and Fl are associated with biomass burning, clearly indicating this factor represented a biomass combustion source (Jenkins et al., 1996; Li et al., 2019). For the second factor, BaA, Chr, BkF, BaP, Phe and IcdP had also relatively high contributions. Of these species, BaA, Chr, and BaP are markers of a coal combustion source (Simcik et al., 1999). In addition, BbF and BghiP are components of fossil fuels and a portion of them are associated with their combustion (Kavouras et al., 2001). Consequently, the second factor can be identified as a fossil fuel combustion source. The third factor was predominated by BghiP, DbahA, IcdP (Gasoline), Ace, Ant, BbF and BkF (Diesel), which are associated with traffic emission (Fraser et al., 1997). The fourth factor was highly related to BbF, which are the indicators of emissions from coke oven (Duval and Friedlander, 1981). The results of PMF analysis showed that PAHs from the vehicle emissions gradually increased from 2014 to 2018. In the other hand, PAHs from the Biomass combustions were decreased from 2015. The number of cars registered in Korea increased from 17.33 million in 2010 to 23.2 million in 2018. With the increasing number of vehicles, the pyrogenic sources of PAHs were dominated with vehicle emissions.

The diagnostic ratios between individual PAHs were applied to identify the sources of 15 PAHs measured in this study. The equation Ant/(Ant + Phe) gave information about petrogenic or pyrogenic origin while the equation BaP/BghiP ratios gave information about traffic or non-traffic origin (Tobiszewski and Namieśnik, 2012) (Figure 14). The equation Ant/(Ant + Phe) showed the dominance

of pyrogenic sources after year 2015. These findings could be explained that the input of atmospheric pollutants from combustion and manufacturing processes were the major contributors of 15 PAHs pollutants in sediments from the west coast of Korea (Choi et al., 2011; Jeon et al., 2017). According to BaP/BghiP ratios, outer regions of LS, SG, and GG were mostly influenced by traffic. This result indicates that combustion origin of 15 PAHs was the greatest at a site with traffic density. Also, 15 PAHs could be introduced into the estuarine and coastal areas through the atmosphere and then adsorbed onto suspended particles or sediments in coastal areas. The concentrations of 15 PAHs in all sediment samples were lower than interim sediment quality guidelines (ISQGs) recommended by CCME (Canadian sediments and soil quality guidelines, 1999).

Styrene trimers (STs)/styrene dimers (SDs) ratios are used as an indicator of polystyrene plastic pollution sources in sediments (Hong et al., 2016a). The higher ratios of STs in sediments indicates a fresh input of 10 SOs because SDs would be detected after decomposition of STs (Kwon et al., 2014; Yoon et al., 2017). In 2010, fresh inputs of 10 SOs existed in all sites. However, the inputs of SOs have decreased over the time and eventually there were no new inputs found in 2018 (Figure 15). Temporal decreases of STs/SDs ratios might be attributed to changes in multiple sources of 10 SOs contamination in sediments of the west coast Korea or specific decomposition mechanism of polystyrene at nearby sources. A recent study reported by Hong et al. (2016) first analyzed 10 SOs in lake and coastal sediments from Lake Sihwa (same as present study) with also relatively great contributions of SDs. Otherwise the analyzed in sediments from the Geum River estuary and Saemangeum coast reported by Yoon et al. (2017) relatively great contributions of STs. These differences of 10 SOs composition might be explained by the site specific sources. Overall, limited information is available on distributions of 10 SOs, thus, more studies are desirable to identify their sources and fate.

Nonylphenolic compounds (nonylphenol, nonylphenol monoethoxylate (NP1EO) and nonylphenol diethoxylate(NP2EO)) determined in this study are biodegradation product of nonylphenol polyethoxylates (NPnEOs) in the marine environment. Nonylphenol polyethoxylates are used in detergents and surfactants. Thus, nonylphenolic chemicals are transported to marine environment from land use through creeks, rivers and sewage effluents. The sum concentrations of NP1EO and NP2EO and the concentrations of NP ratios can be used to index of identifying the new inputs of NPs. The greater contributions of parent compounds suggested the fresh inputs of compounds (Li et al., 2008). (NP1EO + NP2EO)/NPs in sediment samples tended to decrease from 2010 to 2018, which indicated that effective result of regulations from Korean government (Figure 16 and Figure 17). Nevertheless, there were still fresh inputs in a more recent year at SG1 in 2015, AS2 in 2017, and YS2 in 2017. Although 3 NPs in sediments from the west coast Korea were below the interim marine sediment quality guidelines, continuous monitoring of distributions of 3 NPs in sediments will be needed (CCME, 2002).

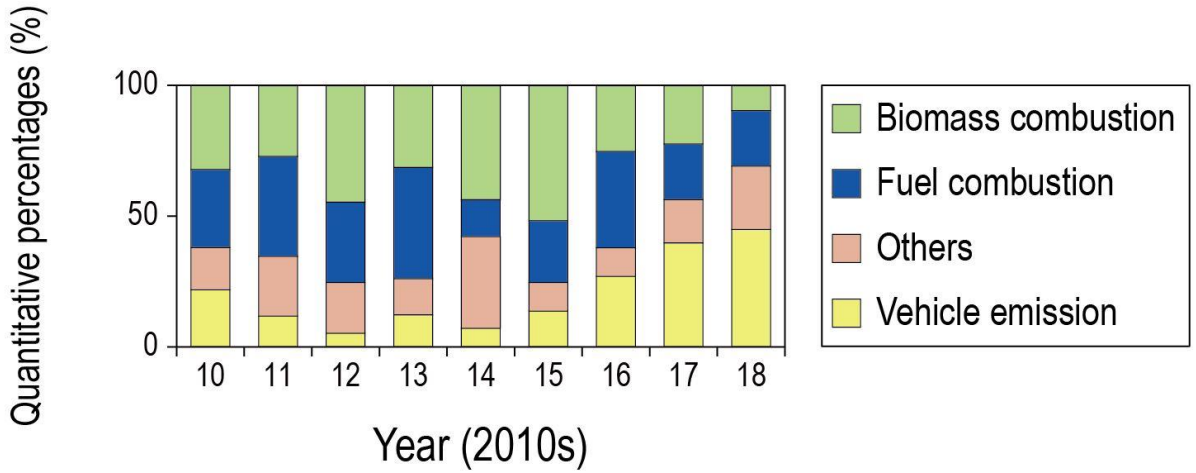


Figure 13. Annual changes of quantitative percentages of PAHs compounds in sediment samples.

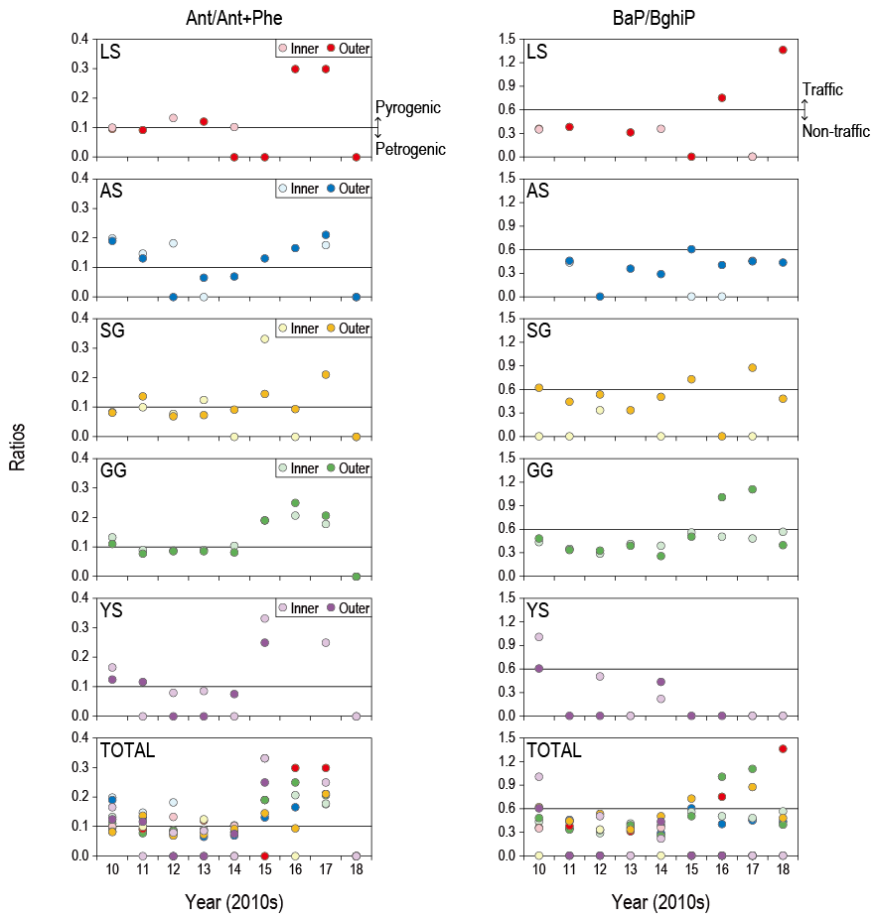


Figure 14. Diagnostic ratios for prediction of sources of chemicals between Ant/(Ant+Phe) and BaP/BghiP.

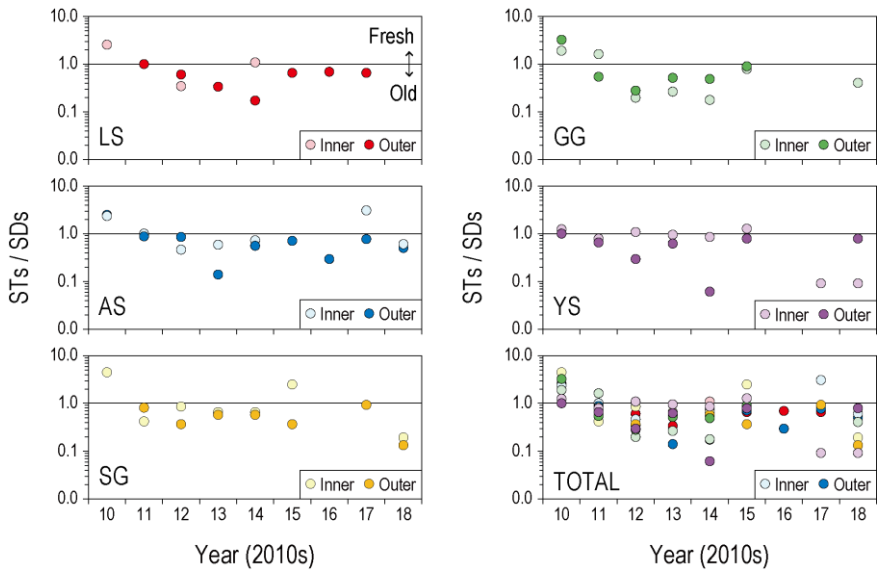


Figure 15. Diagnostic ratios for prediction of fresh input of SOs

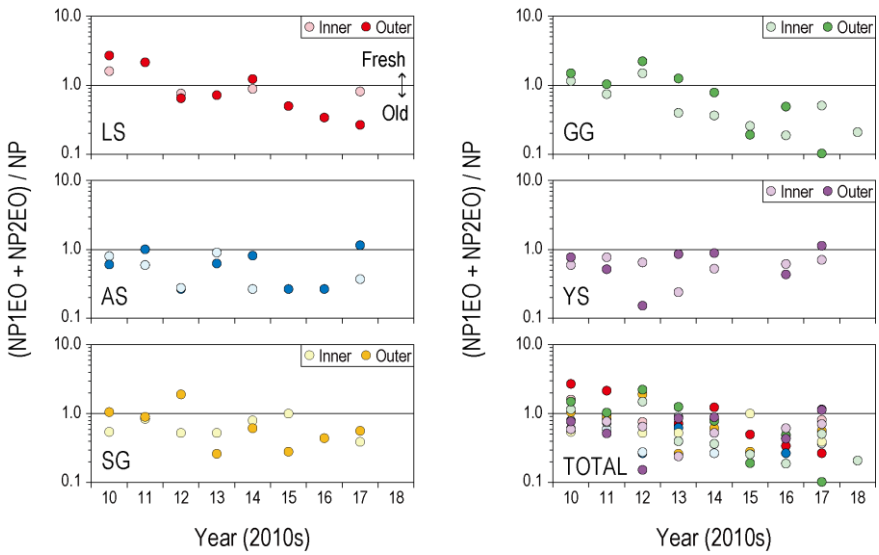


Figure 16. Diagnostic ratios for prediction of fresh input of NPs.

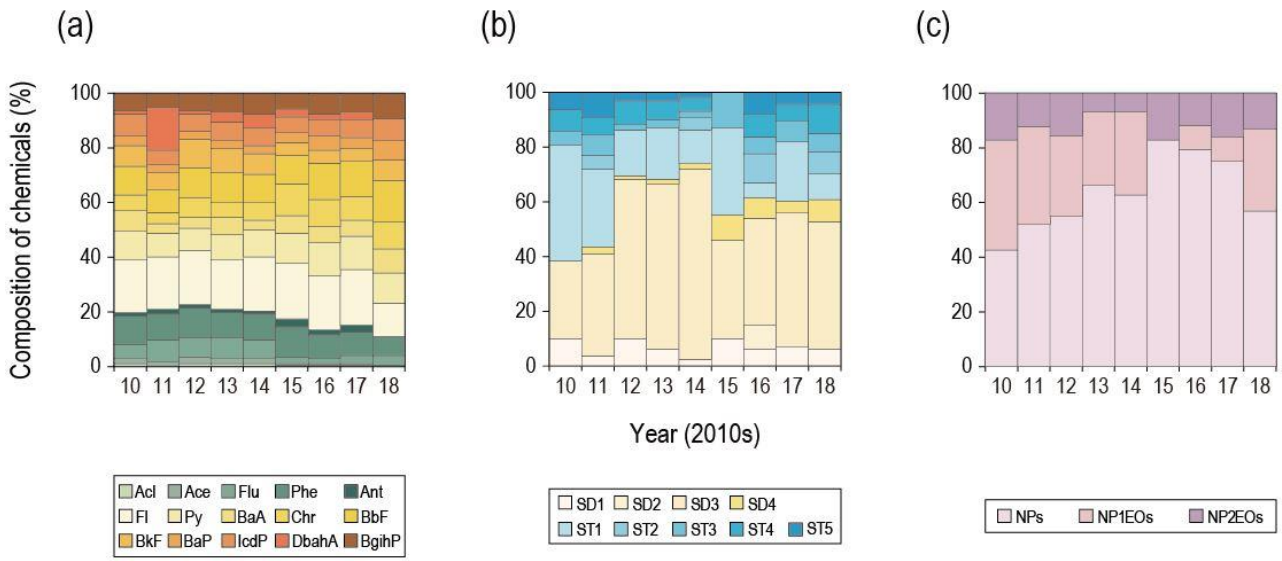


Figure 17. Relative compositions of (a) 15 PAHs, (b) 10 SOs, and (c) 3 NPs.

3.3 Long-term changes of potential biological activities

3.3.1 Dioxin-like and estrogenic activities

The magnitude of AhR-mediated potencies ranged from not detected (n.d.) to 176.2%BaP_{max}. The annual mean variations of AhR-mediated potencies were 99.7%BaP_{max} in 2010, 91.6%BaP_{max} in 2011, 110.9%BaP_{max} in 2012, 123.4%BaP_{max} in 2013, 112.9%BaP_{max} in 2014, 99.5%BaP_{max} in 2015, 83.2%BaP_{max} in 2016, 74.0%BaP_{max} in 2017, and 89.1%BaP_{max} in 2018, respectively. The annual variations of AhR-mediated potencies from 2010 to 2018 did not show significant differences. It has been suggested that there were continuous inputs of AhR-active compounds in sediments from the west coast of Korea (Figure 18).

The mean magnitudes of %BaP_{max} were 70.7%BaP_{max} at LS1, 116.9%BaP_{max} at LS2, 67.6%BaP_{max} at AS1, 124.5%BaP_{max} at AS2, 72.8%BaP_{max} at SG1, 112.7%BaP_{max} at SG2, 129.5%BaP_{max} at GG1, 128.1%BaP_{max} at GG2, 85.5%BaP_{max} at YS1, and 61.3%BaP_{max} at YS2. The mean magnitudes of %BaP_{max} was great at GG1 followed by GG2, where the concentrations of 15 PAHs were also greater than other sites. In addition, %BaP_{max} in the outer regions showed statistically greater than those of inner regions. These results were same patterns of 15 PAHs concentrations in sediment samples (Figure 19). These findings indicated that 15 PAHs targeted in this study could be major AhR-agonists in sediments from the west coast Korea.

The magnitude of ER-mediated potencies ranged from not detected (n.d.) to 82.3%$E2_{max}$. The annual mean variations of AhR-mediated potencies were 7.4%$E2_{max}$ in 2010, 2.9% $E2_{max}$ in 2011, 11.2% $E2_{max}$ in 2012, 14.4% $E2_{max}$ in 2013, 22.5%$E2_{max}$ in 2014, 6.1%$E2_{max}$ in 2015, 4.4%$E2_{max}$ in 2016, and 9.4% $E2_{max}$ in 2017, respectively (Figure 20). The annual variations of ER-mediated potencies from 2010

to 2018 did not show significant differences. It has been suggested that there were continuous inputs of ER-active compounds in sediments from the west coast of Korea The results of monitoring over the past 9 years indicated that the magnitudes of $\%E2_{max}$ have decreased since 2014, which indicated that estrogenic compounds were continuously reduced in the west coast Korea.

The mean magnitudes of $\%E2_{max}$ were $5.6\%E2_{max}$ at LS1, $9.4\%E2_{max}$ at LS2, $3.6\%E2_{max}$ at AS1, $8.8\%E2_{max}$ at AS2, $9.8\%E2_{max}$ at SG1, $10.4\%E2_{max}$ at SG2, $16.3\%E2_{max}$ at GG1, $13.2\%E2_{max}$ at GG2, $11.3\%E2_{max}$ at YS1, and $9.0\%E2_{max}$ at YS2. Temporarily increased $\%E2_{max}$ has been showed at GG1 in 2014 and at YS1 in 2017 (Figure 21). These findings were unlike with the distribution patterns of 3 NPs concentrations, which suggested that other untargeted ER-active compounds are present in sediments of the west coast Korea. The mean $\%E2_{max}$ were no significantly differences between the inner and outer regions. Thus, it is necessary to analyze whether unknown toxic compounds contribute to integrated sample toxicities.

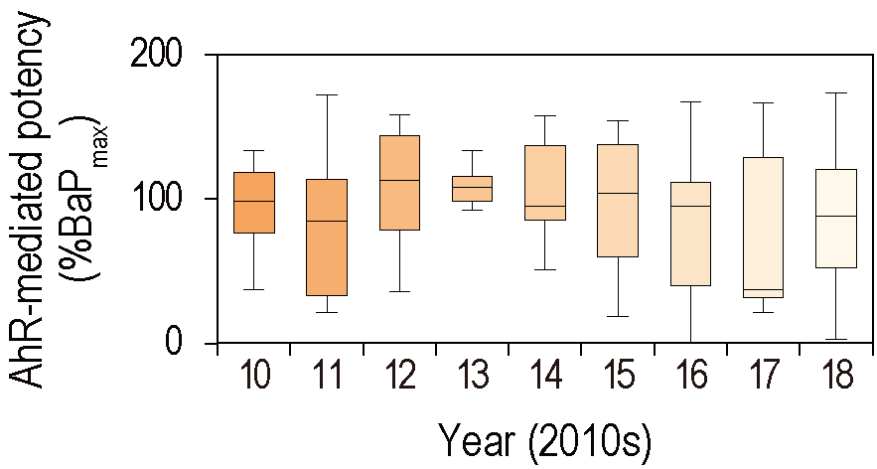


Figure 18. Annual variations in $\%BaP_{max}$ during 2010 to 2018.

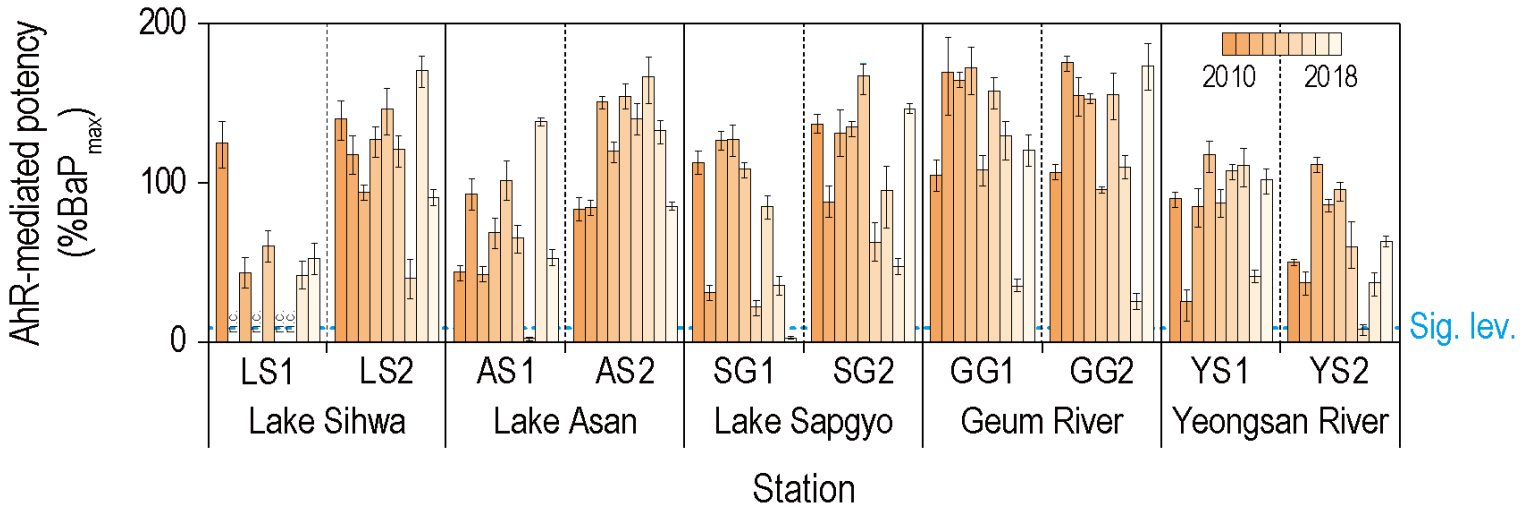


Figure 19. AhR-mediated potencies using the H4IIE-*luc* bioassay elicited by sediments from 2010 to 2018.

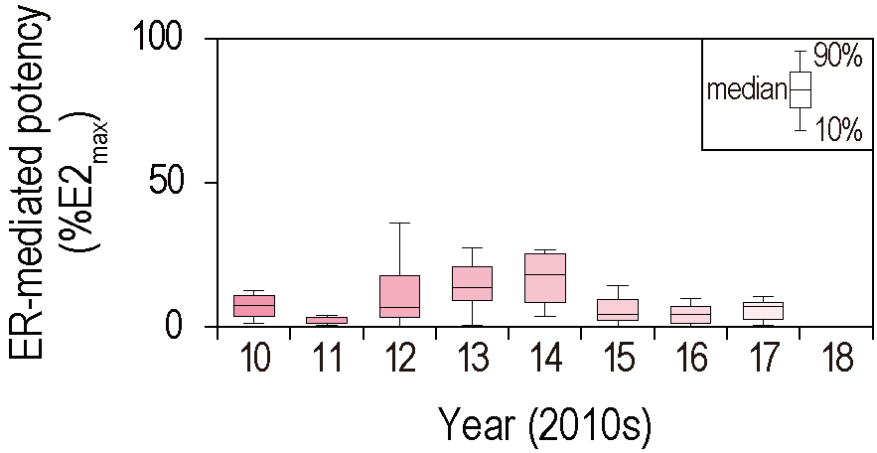


Figure 20. Annual variations in $\%E2_{max}$ during 2010 to 2017.

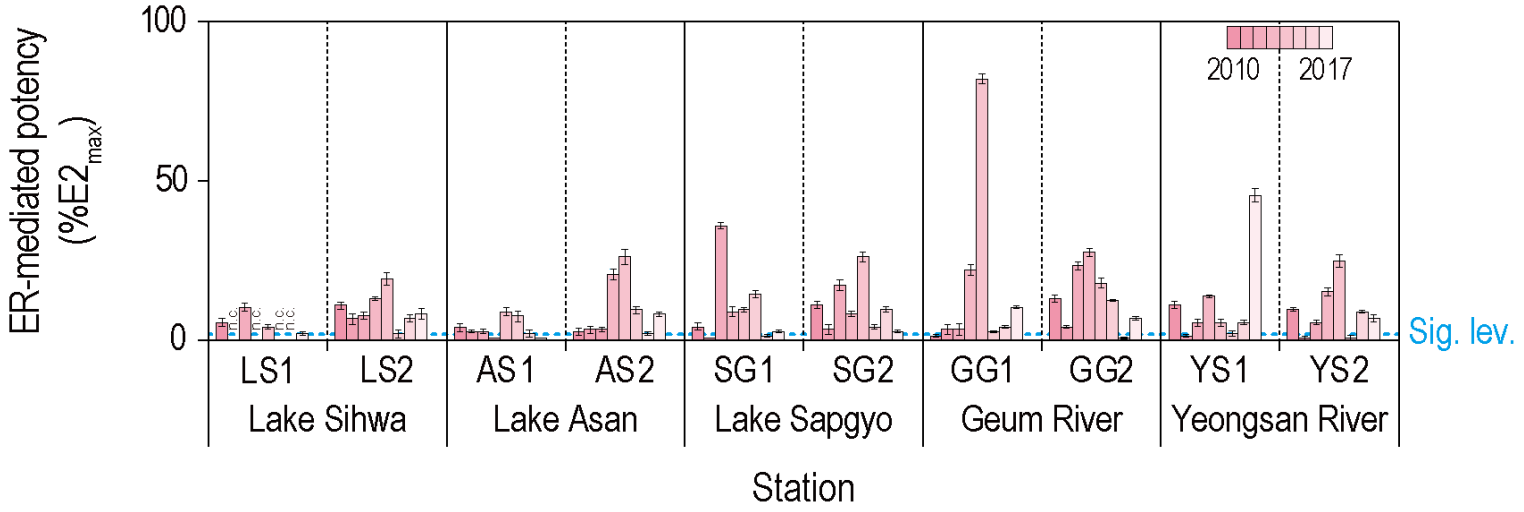


Figure 21. ER-mediated potencies using the MVLN bioassay elicited by sediments from 2010 to 2017.

3.3.2 Bioluminescent inhibition assay

V. fischeri has been widely used as a sensitive tool for monitoring soil and sediment toxicities, considering experimental speed and cost (An et al., 2012; Frana et al., 2013; Parvez et al., 2006). The magnitude of luminescence inhibition rates ranged from not detected (n.d.) to 88.5%. Luminescence inhibition rates were not detected in some sites between 2010 and 2012, but the inhibition rates were shown in all sites after 2012 (Figure 22). The mean luminescence inhibition rates were 2.1% in 2010, 9.9% in 2011, 21.7% in 2012, 44.5% in 2013, 40.6% in 2014, 44.5% in 2015, 32.3% in 2016, 37.8% in 2017, and 338.2% in 2018, respectively (Figure 22). The mean luminescence inhibition rates increased from 2010 to 2013 and then decreased since 2016.

The mean magnitudes of mean luminescence inhibition rates were 21.9% at LS1, 17.3% at LS2, 30.9% at AS1, 26.0% at AS2, 18.8% at SG1, 36.0% at SG2, 40.0% at GG1, 40.8% at GG2, 35.4% at YS1, and 29.8% at YS2 (Figure 23). The great mean inhibition rates were measured at GG1 followed by GG2. Given that GG1 and GG2, which had the greatest concentrations of Cr, Pb, Ni, As, Hg, and Cd the concentration of HMs in sediments could affect coastal organisms (Gao et al., 2018; Islam et al., 2015). In particular, luminescence inhibition rates in GG1 were increased from 2015 to 2018, which indicated that untargeted compounds can cause a toxic effect to *V. fischeri.* These findings indicated that further investigate with untargeted compounds in this study is needed.

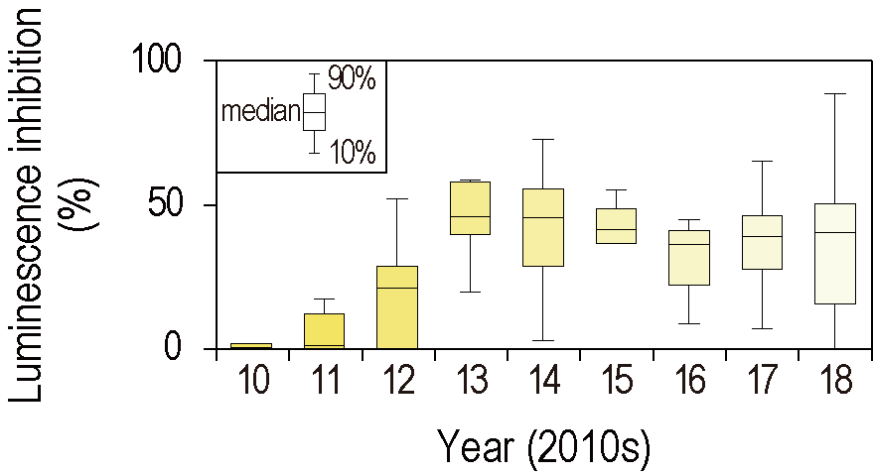


Figure 22. Annual variations of luminescence inhibition rates during 2010 to 2018.

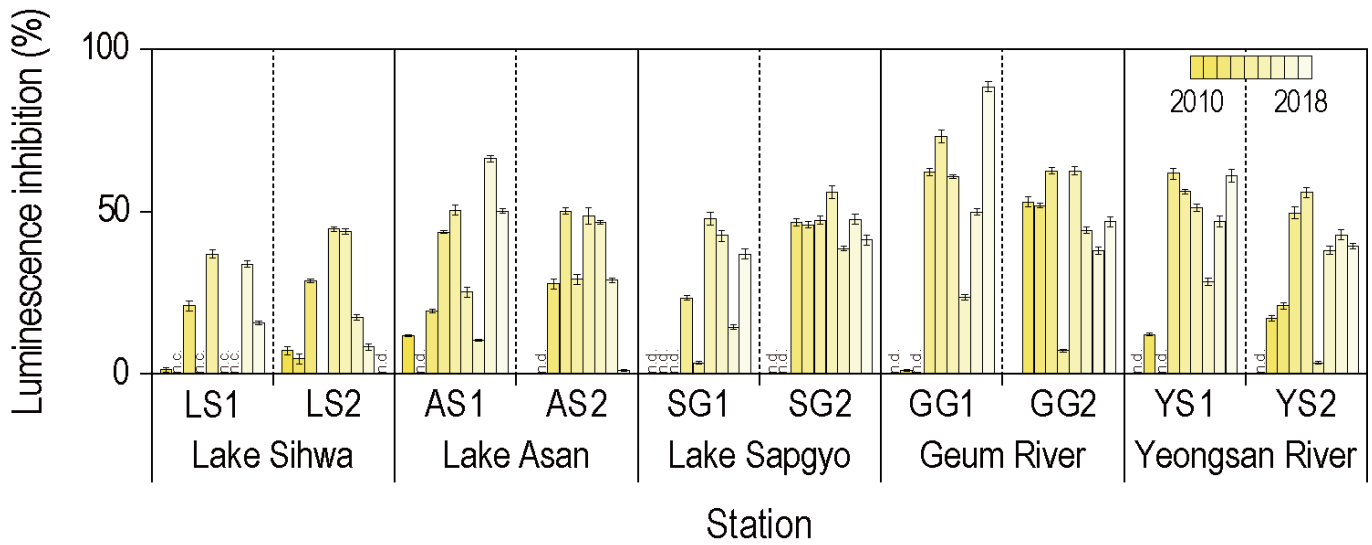


Figure 23. Bioluminescence inhibition rates by *V. fischeri* in elicited by sediments from 2010 to 2018.

3.4 Relationship between chemical analyses and biological responses in sediments

The concentrations of 15 PAHs and AhR-mediated potencies in sediment samples showed a significant correlation (p <0.01) (Figure 24). In particular, relatively great correlations between 15 PAHs concentration and AhR-mediated potencies measured at AS and SG. The concentrations of 3 NPs and ER-mediated potencies in sediment samples were also showed a statistically significant correlation (p <0.01). Relatively great correlation results were found in GG, which regions were the greatest contaminated by PTSs analyzed in this study. The greater concentrations of 15 PAHs and 3 NPs in the west coast sediments have also shown greater potential toxic effects to marine organisms than lower concentrations. The correlation between concentrations of 8 HMs and *V. fischeri* luminescence inhibition rates showed the greatest correlations with Cd concentrations (p <0.01). The results of correlation analysis among the concentrations of 8 individual HMs and the bioassay results are provided in Table 5. In addition, Cd might interact with other chemicals and this put organisms in aquatic environments at risk from their integrated effects (Wang et al., 2009). The correlations between *V. fischeri* luminescence inhibition rates and the concentrations of Cd were the greatest at GG. The greater concentrations of PTSs could have potential toxic effects not only on MVLN and H4IIE-*luc* cells but also on *V. fischeri* luminescence mechanisms. The correlation between concentrations of PTSs and the results of the assessment of biological effects showed regional differences, but there was no difference in annual correlations.

Comparison between results of bioassays and instrumental analysis to identify the contribution of each known chemical in sediments to the overall induced toxic potencies can be performed by potency balance analyses (Giesy et al., 2002; Hong et al., 2012a; Jeon et al., 2017; Khim et al., 2001b).

A potency balance analyses between H4IIE-*luc*-derived BaP-EQ and PAHs and SOs derived BEQ was conducted to determine contributions of AhR-active target PAHs and SOs in this study. Contributions of target AhR agonists in sediments were variable due to the sample-specific chemical compositions. Overall trends of major AhR agonists in sediments along the west coast of Korea were determined using mean concentrations of instrument-derived BEQ and bioassay-derived BaP-EQs of all sediments. The proportion of BaP-EQ accounted for approximately below the 1% of the BEQ, based on the concentrations of PAHs and SOs in sediments (Figure 25). SD3 was the predominant contributor to the BEQ, followed by Py and IcdP. The proportions of BaP-EQ explained by measured chemicals varied among sediments and years. Otherwise a potency balance analyses between MVLN derived E2-EQ and NPs derived EEQs was conducted to determine contributions of ER-active NPs in this study. The proportion of E2-EQ accounted for approximately 0% of the EEQ, based on the concentrations of NPs in sediments. Results of potency balances indicated that target pollutants in this study represented little portion of total AhR and ER-mediated potencies in sediments. This result suggested that untargeted AhR and ER-active compounds were commonly distributed along the west coast of South Korea. Thus, it is necessary to identify the major AhR and ER agonists in sediments.

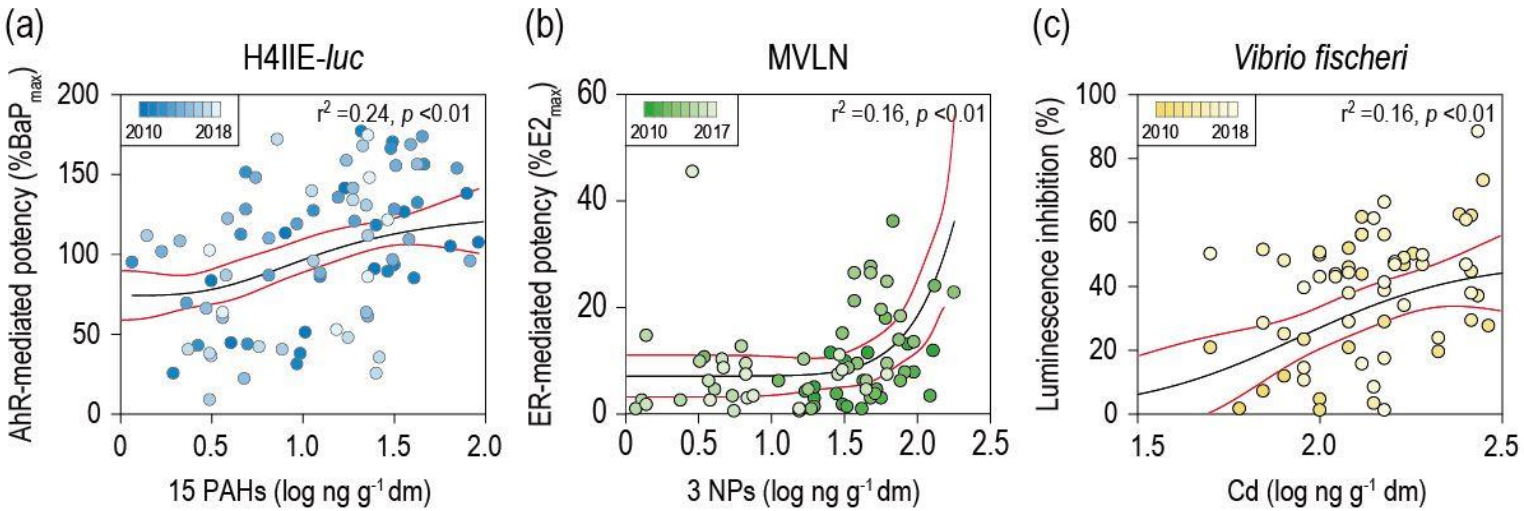


Figure 24. Relationships between bioassays and chemical analyses results. (a) Log concentrations of 15 PAHs vs. AhR-mediated potencies, (b) log concentrations of 3 NPs vs. ER-mediated potencies and (c) log concentrations of Cd vs. luminescence inhibitions.

Table 5. Spearman correlation analysis results among HMs concentrations and potential toxicities in sediments of the west coast, Korea.

		Heavy metals							
		Cr	**Cu**	**Pb**	**Ni**	**Cd**	**As**	**Hg**	**Zn**
Heavy metals	**Cr**								
	Cu	-0.02							
	Pb	0.36**	0.12						
	Ni	0.86**	0.11	0.35**					
	Cd	0.31**	0.33**	0.30**	0.35**				
	As	0.32**	0.19	0.15	0.54**	0.28**			
	Hg	0.62**	0.09	0.44**	0.54**	0.38**	- 0.00		
	Zn	-0.06	0.90**	0.11	0.06	0.26*	0.16	0.03	
Bioassays	**Luminescence inhibition**	0.18	-0.16	0.08	0.15	0.42**	0.11	0.04	-0.21*

* = Significant correlation at the level of 0.05, ** = Significant correlation at the level of 0.01

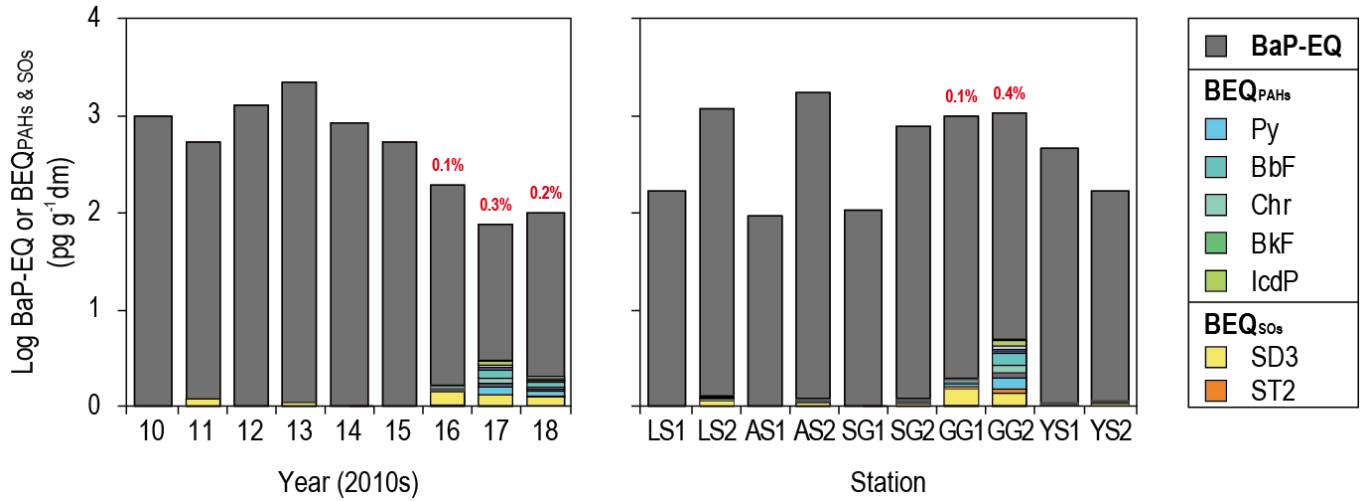


Figure 25. Annual and regional variations of BaP-EQs and BEQs.

3.5 Temporal trends of sedimentary pollution in the coastal area resulted from environmental regulations

The Ministry of Environment conducts an annual survey on the amount of chemicals emitted from factories to minimize environmental pollution through efforts to reduce emissions (http://icis.me.go.kr). In addition, in order to regulate the production and use of POPs, the Ministry of Environment collects POPs from all over the country every year. There is no emission survey data of PAHs, so the detection amounts of the PCDD/DFs, which are same AhR agonist like PAHs were compared with the concentrations flow of PAHs analyzed in this study (Figure 26a). The concentrations of terrestrial PCDD/DF decreased from 51 ng TEQ m^{-3} in 2009 to 24 ng TEQ m^{-3} in 2016. 15 PAHs concentrations in west coast sediments also tend to decrease after 2010 meaning that management of terrestrial dioxin-like compounds can affect the coastal environments. For more accurate management, measurements of PAHs emission amounts are required.

The change in annual polystyrene consumption (European Plastic and Rubber Association, Euromap, 2016) and the concentrations of SOs in west coast sediments were compared (Figure 26b). From 2009 to 2016, poly styrene consumptions tended to increase, but the concentrations of SOs in sediments decrease after 2014. Although there was no immediate effect from the consumption of SOs in land to the concentration in offshore deposits, it is needed to identify the relationship between the polystyrene concentration in land and the concentration in coastal areas then regulate and control the pollutants effectively. To do this, it seems to be necessary to measure the emission amounts of terrestrial poly styrene.

Changes in terrestrial NPs emission amounts and 3 NPs in sediments showed similar annual patterns (Figure 26c). The annual variation patterns of concentrations between terrestrial and coastal compounds were similar with no time differences. Despite the ban on using NPs in 2010, NPs emission amounts temporarily increased, but have since shown a steady decrease in concentrations after 2015 when industrial applications were prohibited (Figure 26c). The results from the success of chemical controls and regulations by the Korean government, both terrestrial emission amounts and concentrations of NP in sediments tend to decrease.

In HMs, terrestrial emission amounts and concentrations in sediments were not show similar variation patterns except for those of Cd (Figure 26). Cd concentrations have shown a steady decline in terrestrial emission amounts since 2010. The concentrations of Cd in sediments were below the TEL (MOF, 2013) except 2014. In the case of Cd, the annual variation patterns of terrestrial emission amounts were similar to those of concentrations in sediments after 4 years. This might be the results of HMs emitted from the inland do not reach the coastal environments yet or the changes of concentrations because of direct HMs introductions in the coastal environments. To date, there have been very few studies assess the effects of pollutant policies by comparing the amounts of pollutant emissions in land and concentrations in sediments. Future studies will be needed to assess whether efforts to reduce pollutant emissions lead to the reduction of pollutants in the coastal environments and furthermore, whether these efforts affect the potential or acute toxicities to coastal organisms. In addition, continuous efforts to reduce contaminants will be needed by additionally measuring the emission amounts of persistent pollutants (PAHs, Styrene oligomers) which remain in the coastal environments and are known to affect ecosystems (Daskalakis and O'Connor, 1995; Giesy and Kannan, 1998; Hong et al., 2016; Khim and Hong, 2014).

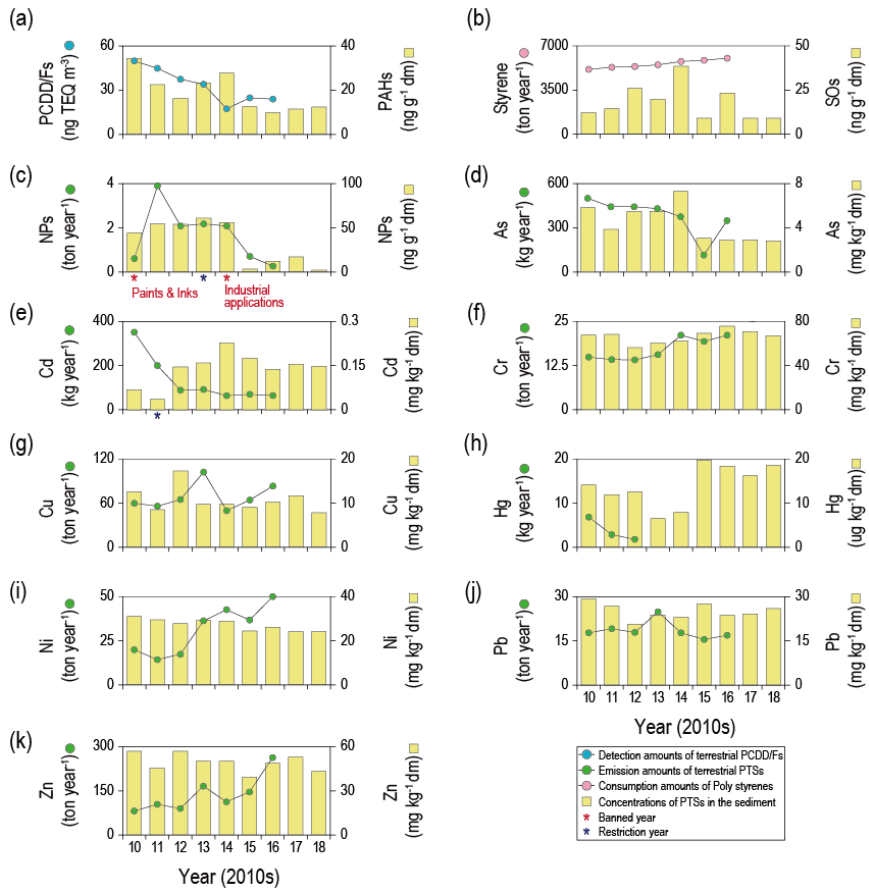


Figure 26. Temporal trends of sedimentary pollution in the terrestrial and coastal area.

Chapter 4. Conclusions

In this study, sediments were collected from the west coast of Korea for nine years from 2010 to 2018 in order to identify spatio-temporal distributions of polycyclic aromatic hydrocarbons (PAHs), styrene oligomers (SOs), nonylphenols (NPs) and heavy metals (HMs) and screen the screen the potential effects of sedimentary pollutants through the bioassays. The concentrations of compounds analyzed in this study were distributed within a range lower than those of international or marine environmental guidelines.

Results of 9-year monitoring of pollutant concentrations in sediments along the west coast of Korea that among the sampling sites, Geum River was found the most polluted region. However, the concentrations of the target compounds were lower than the sediments quality guideline in most sampling sites. The great concentration of PAHs, SOs, NPs, and HMs were 93.5 ng g^{-1} dm, 99.4 ng g^{-1} dm, 176.2 ng g^{-1} dm, and 122 mg kg^{-1}, respectively. Composition ratios of each pollutant concentrations were used to identify the sources of each pollutant. The major sources of PAHs analyzed in this study dominated by pyrogenic sources, especially traffic emissions were relatively great recent years. SOs and NPs have tended to decrease new inputs in study period. These results considered to success of the government's chemical controls and regulations especially for NPs. The results of bioassay showed similar patterns with PTSs concentrations. Also, AhR-mediated potencies and *V. fischeri* luminescence inhibition rates were great in GG than other regions.

The PAH concentrations showed a positive relationship with AhR-mediated potencies (r = 0.53, p <0.01) and so did the NP concentrations with ER-mediated potencies (r = 0.31, p <0.01). Also, Cd concentrations showed significant correlation with bioluminescence inhibition rates of *V. fischeri* (r = 0.47, p <0.01). A potency balance analyses between H4IIE-*luc*-derived BaP-EQ and PAHs and SOs derived BEQ was conducted to determine contributions of AhR-active target PAHs and SOs. Also, between MVLN-derived E2-EQ and NPs derived EEQ was conducted to assess the contribution of each PTSs to biological activities. The proportion of BaP-EQ accounted for approximately below the 1% of the BEQ, based on the concentrations of PAHs and SOs in sediments. The proportion of E2-EQ accounted for approximately 0% of the EEQ, based on the concentrations of NPs in sediments. The result through potency balances indicated that target pollutants in this study represented little portion of total AhR and ER-mediated potencies in sediments along the west coast of Korea for 9 years. It means that unknown AhR and ER- active compounds are commonly distributed in sediments along the west coast of Korea. Thus, it is necessary to find unidentified AhR and ER agonists in west coast sediments and monitor the pollutants continuously.

References

Aksentijević, S., Kiurski, J., Vasić, M.V., 2012. Arsenic distribution in water/sediment system of Sevojno. Environ. Monit. Assess. 184, 335-341.

Ali, B.N.M., Lin, C.Y., Cleophas, F., Abdullah, M.H., Musta, B., 2015. Assessment of heavy metals contamination in Mamut river sediments using sediment quality guidelines and geochemical indices. Environ. Monit. Assess. 187, 4190.

An, J., Jeong, S., Moon, H.S., Jho, E.H., Nam, K., 2012. Prediction of Cd and Pb toxicity to *Vibrio fischeri* using biotic ligand-based models in soil. J. Hazard. Mater. 203, 69-76.

Bulich, A., 1986. Bioluminescence assays, toxicity testing using microorganisms, vol. 1. CRC Press.

Canadian Council of Ministers of the Environment (CCME). 1999. Canadian sediment quality guidelines for the protection of aquatic life: Polycyclic aromatic hydrocarbons (PAHs). In: Canadian environmental quality guidelines, 1999, Canadian Council of Ministers of the Environment, Winnipeg.

Canadian Council of Ministers of the Environment (CCME). 2002. Canadian sediment quality guidelines for the protection of aquatic life: Nonylphenol and its ethoxylates. In: Canadian environmental quality guidelines, 2002, Canadian Council of Ministers of the Environment, Winnipeg.

Chen, C.-W., Kao, C.-M., Chen, C.-F., Dong, C.-D., 2007. Distribution and accumulation of heavy metals in the sediments of Kaohsiung Harbor, Taiwan. Chemosphere 66, 1431-1440.

Choi, H.G., Moon, H.B., Choi, M., Yu, J., 2011. Monitoring of organic contaminants in sediments from the Korean coast: spatial distribution and temporal trends (2001–2007). Mar. Pollut. Bull. 62, 1352-1361.

Christophoridis, C., Dedepsidis, D., Fytianos, K., 2009. Occurrence and distribution of selected heavy metals in the surface sediments of Thermaikos Gulf, N. Greece. Assessment using pollution indicators. Journal of hazardous materials 168, 1082-1091.

Daskalakis, K.D., O'Connor, T.P., 1995. Normalization and elemental sediment contamination in the coastal United States. Environ. Sci. Technol. 29, 470-477.

Dassenakis, M., Andrianos, H., Depiazi, G., Konstantas, A., Karabela, M., Sakellari, A., Scoullos, M., 2003. The use of various methods for the study of metal pollution in marine sediments, the case of Euvoikos Gulf, Greece. Applied Geochemistry 18, 781-794.

Deng, J., Zhang, Y., Qiu, Y., Zhang, H., Du, W., Xu, L., Hong, Y., Chen, Y., Chen, J., 2018. Source apportionment of PM2. 5 at the Lin'an regional background site in China with three receptor models. Atmospheric research 202, 23-32.

Fernandes, M., Sicre, M.-A., Boireau, A., Tronczynski, J., 1997. Polyaromatic hydrocarbon (PAH) distributions in the Seine River and its estuary. Mar. Pollut. Bull. 34, 857-867.

Frana, F., Bebianno, M., Cabral, H., 2013. Evaluation of sediment toxicity in different Portuguese estuaries: ecological impact of metals and polycyclic aromatic hydrocarbons. Estuar. Coast. Shelf Sci. 130, 3041Shipp.

Fraser, M.P., Cass, G.R., Simoneit, B.R., Rasmussen, R., 1997. Air quality model evaluation data for organics. 4. C2− C36 non-aromatic hydrocarbons. Environ. Sci. Technol. 31, 2356-2367.

Gao, L., Wang, Z., Li, S., Chen, J., 2018. Bioavailability and toxicity of trace metals (Cd, Cr, Cu, Ni, and Zn) in sediment cores from the Shima River, South China. Chemosphere 192, 31-42.

Gao, L., Wang, Z., Shan, J., Chen, J., Tang, C., Yi, M., Zhao, X., 2016. Distribution characteristics and sources of trace metals in sediment cores from a trans-boundary watercourse: An example from the Shima River, Pearl River Delta. Ecotoxicology and environmental safety 134, 186-195.

Giesy, J.P., Kannan, K., 1998. Dioxin-like and non-dioxin-like toxic effects of polychlorinated biphenyls (PCBs): implications for risk assessment. Crit. Rev. Toxicol. 28, 511-569.

Giesy, J.P., Hilscherová, K., Jones, P.D., Kannan, K., Machala, M., 2002. Cell bioassays for detection of aryl hydrocarbon (AhR) and estrogen receptor (ER) mediated activity in environmental samples. Mar. Pollut. Bull. 45, 3-16.

Hilscherova, K., Machala, M., Kannan, K., Blankenship, A.L., Giesy, J.P., 2000. Cell bioassays for detection of aryl hydrocarbon (AhR) and estrogen receptor (ER) mediated activity in environmental samples. Environmental Science and Pollution Research 7, 159-171.

Hong, S., Khim, J.S., Naile, J.E., Park, J., Kwon, B.-O., Wang, T., Lu, Y., Shim, W.J., Jones, P.D., Giesy, J.P., 2012a. AhR-mediated potency of sediments and soils in estuarine and coastal areas of the Yellow Sea region: a comparison between Korea and China. Environ. Pollut. 171, 216-225.

Hong, S., Khim, J.S., Ryu, J., Park, J., Song, S.J., Kwon, B.-O., Choi, K., Ji, K., Seo, J., Lee, S., 2012b. Two years after the Hebei Spirit oil spill: residual crude-derived hydrocarbons and potential AhR-mediated activities in coastal sediments. Environ. Sci. Technol. 46, 1406-1414.

Hong, S., Khim, J.S., Wang, T., Naile, J.E., Park, J., Kwon, B.-O., Song, S.J., Ryu, J., Codling, G., Jones, P.D., 2015. Bioaccumulation characteristics of perfluoroalkyl acids (PFAAs) in coastal organisms from the west coast of South Korea. Chemosphere 129, 157-163.

Hong, S., Lee, J., Lee, C., Yoon, S.J., Jeon, S., Kwon, B.-O., Lee, J.-H., Giesy, J.P., Khim, J.S., 2016a. Are styrene oligomers in coastal sediments of an industrial area aryl hydrocarbon-receptor agonists? Environ. Pollut. 213, 913-921.

Hong, S., Yim, U.H., Ha, S.Y., Shim, W.J., Jeon, S., Lee, S., Kim, C., Choi, K., Jung, J., Giesy, J.P., 2016b. Bioaccessibility of AhR-active PAHs in sediments contaminated by the Hebei Spirit oil spill: application of Tenax extraction in effect-directed analysis. Chemosphere 144, 706-712.

Horii, Y., Khim, J.S., Higley, E.B., Giesy, J.P., Ohura, T., Kannan, K., 2009. Relative potencies of individual chlorinated and brominated polycyclic aromatic hydrocarbons for induction of aryl hydrocarbon receptor-mediated responses. Environ. Sci. Technol. 43, 2159-2165.

Islam, M.S., Ahmed, M.K., Raknuzzaman, M., Habibullah-Al-Mamun, M., Islam, M.K., 2015. Heavy metal pollution in surface water and sediment: a preliminary assessment of an urban river in a developing country. Ecol. Indicators 48, 282-291.

Jacobs, M.W., Coates, J.A., Delfino, J.J., Bitton, G., Davis, W.M., Garcia, K.L., 1993. Comparison of sediment extract Microtox® toxicity with semi-volatile organic priority pollutant concentrations. Arch. Environ. Contam. Toxicol. 24, 461-468.

Jeon, S., Hong, S., Kwon, B.-O., Park, J., Song, S.J., Giesy, J.P., Khim, J.S., 2017. Assessment of potential biological activities and distributions of endocrine-disrupting chemicals in sediments of the west coast of South Korea. Chemosphere 168, 441-449.

Kavouras, I.G., Koutrakis, P., Tsapakis, M., Lagoudaki, E., Stephanou, E.G., Von Baer, D., Oyola, P., 2001. Source apportionment of urban particulate aliphatic and polynuclear aromatic hydrocarbons (PAHs) using multivariate methods. Environ. Sci. Technol. 35, 2288-2294.

Ke, X., Gui, S., Huang, H., Zhang, H., Wang, C., Guo, W., 2017. Ecological risk assessment and source identification for heavy metals in surface sediment from the Liaohe River protected area, China. Chemosphere 175, 473-481.

Keith, L. H., Telliard, W. J., 1979. Priority Pollutants I. A Perspective View. Environ. Sci. Technol. 13, 416–423.

Khim, J.S., Lee, K., Kannan, K., Villeneuve, D., Giesy, J., Koh, C., 2001a. Trace organic contaminants in sediment and water from Ulsan Bay and its vicinity, Korea. Arch. Environ. Contam. Toxicol. 40, 141-150.

Khim, J.S., Lee, K., Villeneuve, D., Kannan, K., Giesy, J., Koh, C., 2001b. In vitro bioassay determination of dioxin-like and estrogenic activity in sediment and water from Ulsan Bay and its vicinity, Korea. Arch. Environ. Contam. Toxicol. 40, 151-160.

Khim, J.S., Hong, S., 2014. Assessment of trace pollutants in Korean coastal sediments using the triad approach: a review. Sci. Total Environ. 470, 1450-1462.

Khim, J.S., Villeneuve, D.L., Kannan, K., Lee, K.T., Snyder, S.A., Koh, C.H., Giesy, J.P., 1999. Alkylphenols, polycyclic aromatic hydrocarbons, and organochlorines in sediment from Lake Shihwa, Korea: instrumental and bioanalytical characterization. Environ. Toxicol. Chem. 18, 2424-2432.

Kim, G., Anderson, J.W., Bothner, K., Hyeon Lee, J., Hwan Koh, C., Tanabe, S., 1997. Application of P450RGS reporter gene system as a bioindicator of sediment PAH contamination in the vicinity of Incheon Harbor, Korea. Biomarkers 2, 181-188.

Kim, D.G., Min, Y.K., Jeong, J.Y., Kim, G.H., Kim, J.Y., Son, C.S., Lee, D.H., 2007. Ambient air monitoring of PCDD/Fs and co-PCBs in Gyeonggi-do, Korea. Chemosphere 67, 1722-1727.

Kinani, S., Bouchonnet, S., Creusot, N., Bourcier, S., Balaguer, P., Porcher, J.-M., Aït-Aïssa, S., 2010. Bioanalytical characterisation of multiple endocrine-and dioxin-like activities in sediments from reference and impacted small rivers. Environ. Pollut. 158, 74-83.

Koh, C.H., Khim, J.S., Villeneuve, D.L., Kannan, K., Giesy, J.P., 2002. Analysis of trace organic contaminants in sediment, pore water, and water samples from Onsan Bay, Korea: instrumental analysis and in vitro gene expression assay. Environmental Toxicology and Chemistry: An International Journal 21, 1796-1803.

Koh, C.H., Khim, J.S., Kannan, K., Villeneuve, D.L., Senthilkumar, K., Giesy, J.P., 2004. Polychlorinated dibenzo-p-dioxins (PCDDs), dibenzofurans (PCDFs), biphenyls (PCBs), and polycyclic aromatic hydrocarbons (PAHs) and 2,3,7,8-TCDD equivalents (TEQs) in sediment from the Hyeongsan River, Korea. Environ. Pollut. 132, 489-501.

Koh, C.H., Khim, J.S., Villeneuve, D.L., Kannan, K., Giesy, J.P., 2006. Characterization of trace organic contaminants in marine sediment from Yeongil Bay, Korea: 1. Instrumental analyses. Environ. Pollut. 142, 39-47.

Koniecko, I., Staniszewska, M., Falkowska, L., Burska, D., Kielczewska, J., Jasinska, A., 2014. Alkylphenols in surface sediments of the Gulf of Gdansk (Baltic Sea). Water, Air, Soil Pollut. 225, 2040.

Kwon, B.G., Saido, K., Koizumi, K., Sato, H., Ogawa, N., Chung, S.-Y., Kusui, T., Kodera, Y., Kogure, K., 2014. Regional distribution of styrene analogues generated from polystyrene degradation along the coastlines of the North-East Pacific Ocean and Hawaii. Environ. Pollut. 188, 45-49.

Lee, E., Chan, C.K., Paatero, P., 1999. Application of positive matrix factorization in source apportionment of particulate pollutants in Hong Kong. Atmos. Environ. 33, 3201-3212.

Lee, J., Hong, S., Yoon, S.J., Kwon, B.-O., Ryu, J., Giesy, J.P., Allam, A.A., Al-Khedhairy, A.A., Khim, J.S., 2017a. Long-term changes in distributions of dioxin-like and estrogenic compounds in sediments of Lake Sihwa, Korea: Revisited mass balance. Chemosphere 181, 767-777.

Lee, S., Chung, J., Kim, C., Lee, Y.-W., 2017b. Distribution of Heavy Metals in Korean Coastal Areas Correlated to Emission from Industrial Operations. Environmental Engineering Science 34, 569-576.

Li, D., Dong, M., Shim, W.J., Yim, U.H., Hong, S.H., Kannan, N., 2008. Distribution characteristics of nonylphenolic chemicals in Masan Bay environments, Korea. Chemosphere 71, 1162-1172.

Li, H., Yu, S., Li, G., Deng, H., 2012. Lead contamination and source in Shanghai in the past century using dated sediment cores from urban park lakes. Chemosphere 88, 1161-1169.

Liu, C.-W., Liang, C.-P., Lin, K.-H., Jang, C.-S., Wang, S.-W., Huang, Y.-K., Hsueh, Y.-M., 2007. Bioaccumulation of arsenic compounds in aquacultural clams (Meretrix lusoria) and assessment of potential carcinogenic risks to human health by ingestion. Chemosphere 69, 128-134.

Macikova, P., Kalabova, T., Klanova, J., Kukucka, P., Giesy, J., Hilscherova, K., 2014. Longer-term and short-term variability in pollution of fluvial sediments by dioxin-like and endocrine disruptive compounds. Environmental Science and Pollution Research 21, 5007-5022.

Moon, H.B., Kim, S.S., 2001. Level and origin of polycyclic aromatic hydrocarbons (PAHs) in sediments from Ulsan Bay, Korea. Environmental Science 10, 113-119.

Naile, J.E., Khim, J.S., Wang, T., Chen, C., Luo, W., Kwon, B.O., Park, J., Koh, C.-H., Jones, P.D., Lu, Y., Giesy, J.P., 2010. Perfluorinated compounds inwater, sediment, soil and biota from estuarine and coastal areas of Korea. Environ. Pollut. 158, 1237-1244.

Naile, J.E., Khim, J.S., Wang, T., Wan, Y., Luo, W., Hu, W., Jiao, W., Park, J., Ryu, J., Hong, S., 2011. Sources and distribution of polychlorinated-dibenzo-p-dioxins and-dibenzofurans in soil and sediment from the Yellow Sea region of China and Korea. Environ. Pollut. 159, 907-917.

Nicolás, J., Chiari, M., Crespo, J., Orellana, I.G., Lucarelli, F., Nava, S., Pastor, C., Yubero, E., 2008. Quantification of Saharan and local dust impact in an arid Mediterranean area by the positive matrix factorization (PMF) technique. Atmos. Environ. 42, 8872-8882.

Noh, J., Yoon, S.J., Lee, C., Kwon, B.-O., Khim, J.S.m 2018. Optimal Environmental Monitoring System for Ecosystem Assessment in the Geum River Estuary, Korea. J. Korean Soc. Mar. Environ. Energy 21, 334-350.

Nriagu, J.O., 1996. A history of global metal pollution. Science 272, 223-223.

Ohyama, K., Nagai, F., Tsuchiya, Y., 2001. Certain styrene oligomers have proliferative activity on MCF-7 human breast tumor cells and binding affinity for human estrogen receptor. Environ. Health Perspect. 109, 699-703.

Parvez, S., Venkataraman, C., Mukherji, S., 2006. A review on advantages of implementing luminescence inhibition test (*Vibrio fischeri*) for acute toxicity prediction of chemicals. Environ. Int. 32, 265-268.

Roman, Y.E., De Schamphelaere, K.A., Nguyen, L.T., Janssen, C.R., 2007. Chronic toxicity of copper to five benthic invertebrates in laboratory-formulated sediment: Sensitivity comparison and preliminary risk assessment. Sci. Total Environ. 387, 128-140.

Ryu, J., Hong, S., Chang, W.K., Khim, J.S., 2016. Performance evaluation and validation of ecological indices toward site-specific application for varying benthic conditions in Korean coasts. Sci. Total Environ. 541, 1161-1171.

Soares, A., Guieysse, B., Jefferson, B., Cartmell, E., Lester, J., 2008. Nonylphenol in the environment: a critical review on occurrence, fate, toxicity and treatment in wastewaters. Environ. Int. 34, 1033-1049.

Taylor, S., 1964. Abundance of chemical elements in the continental crust: a new table. Geochim. Cosmochim. Acta 28, 1273-1285.

Tobiszewski, M., Namieśnik, J., 2012. PAH diagnostic ratios for the identification of pollution emission sources. Environ. Pollut. 162, 110-119.

Varol, M., 2011. Assessment of heavy metal contamination in sediments of the Tigris River (Turkey) using pollution indices and multivariate statistical techniques. J. Hazard. Mater. 195, 355-364.

Villeneuve, D.L., DeVita, W.M., Crunkilton, R.L., 1998. Identification of cytochrome P4501A inducers in complex mixtures of polycyclic aromatic hydrocarbons. ASTM special technical publication 1333, 92-104.

Villeneuve, D.L., Khim, J.S., Kannan, K., Giesy, J.P., 2002. Relative potencies of individual polycyclic aromatic hydrocarbons to induce dioxinlike and estrogenic responses in three cell lines. Environ. Toxicol. 17, 128-137.

Wang, W., Lampi, M.A., Huang, X.D., Gerhardt, K., Dixon, D.G., Greenberg, B.M., 2009. Assessment of mixture toxicity of copper, cadmium, and phenanthrenequinone to the marine bacterium *Vibrio fischeri*. Environmental Toxicology: An International Journal 24, 166-177.

Yoon, S.J., Hong, S., Kwon, B.-O., Ryu, J., Lee, C.-H., Nam, J., Khim, J.S., 2017. Distributions of persistent organic contaminants in sediments and their potential impact on macrobenthic faunal community of the Geum River Estuary and Saemangeum Coast, Korea. Chemosphere 173, 216-226.

Zhang, Y., Guo, C.-S., Xu, J., Tian, Y.-Z., Shi, G.-L., Feng, Y.-C., 2012. Potential source contributions and risk assessment of PAHs in sediments from Taihu Lake, China: comparison of three receptor models. Water Res. 46, 3065-3073.

Zhang, Z., Lu, Y., Li, H., Tu, Y., Liu, B., Yang, Z., 2018. Assessment of heavy metal contamination, distribution and source identification in the sediments from the Zijiang River, China. Sci. Total Environ. 645, 235-243.

Appendix

Appendix 1. Individual PAHs concentration in sediment from sampling sites.

Sampling		PAHs concentrations (ng g^{-1} dm)															
Location	Year	Acl	Ace	Flu	Phe	Ant	Fl	Py	BaA	Chr	BbF	BkF	BaP	IcdP	DbahA	BghiP	Total
LS1	2017	<DL	<DL	<DL	<DL	<DL	<DL	0.2	<DL	<DL	<DL	<DL	<DL	<DL	<DL	0.2	0.4
	2018	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	0.0
LS2	2015	<DL	<DL	<DL	0.3	<DL	0.6	0.3	0.4	0.6	<DL	<DL	<DL	0.3	<DL	0.2	2.7
	2016	<DL	<DL	<DL	0.7	0.3	2	1	0.4	0.9	1	<DL	0.3	0.4	<DL	0.4	7.4
	2017	<DL	<DL	<DL	0.7	0.3	1.6	0.9	0.4	1.1	0.7	<DL	<DL	0.3	<DL	0.4	6.4
	2018	<DL	<DL	<DL	1.3	<DL	2.3	2.4	2.1	<DL	2.2	0.8	1.9	1	<DL	1.4	15.4
AS1	2015	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	0.4	0.6	0.3	1.3
	2016	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	0.3	0.2	0.5
	2017	<DL	<DL	<DL	1.4	0.3	1.8	1.3	0.5	1	0.7	0.6	0.5	0.9	0.9	1.1	11.0
	2018	<DL	<DL	<DL	0.5	<DL	<DL	0.3	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	0.8
AS2	2015	<DL	<DL	<DL	3.3	0.5	3.3	1.5	1.2	2.3	1.7	1	0.6	1.2	1.2	1	18.8
	2016	<DL	<DL	<DL	2	0.4	4.5	2.3	1.2	2.6	2.6	1	0.8	1.3	0.6	2	21.3
	2017	<DL	<DL	<DL	1.5	0.4	3.1	2	1.1	1.6	2.8	0.5	0.9	1.8	0.8	2	18.5
	2018	<DL	<DL	<DL	1.7	<DL	2.8	2.8	1.2	1.5	4.9	1.7	1.3	2.3	<DL	3	23.2
SG1	2015	<DL	<DL	<DL	0.4	0.2	1.2	0.5	<DL	0.7	<DL	0.5	<DL	<DL	<DL	<DL	3.5
	2016	<DL	<DL	<DL	0.6	<DL	1	0.9	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	2.5
	2017	<DL	<DL	<DL	<DL	<DL	0.7	0.4	<DL	<DL	<DL	<DL	<DL	<DL	<DL	0.2	1.3
	2018	<DL	<DL	<DL	0.4	<DL	<DL	0.2	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	0.6

SG2	2015	<DL	0.3	0.6	3.5	0.6	5.2	2.4	1.2	2.4	2.2	0.9	0.8	1.1	0.3	1.1	22.6
	2016	<DL	<DL	<DL	1.9	0.2	2.7	3	0.5	0.7	1.4	<DL	<DL	<DL	<DL	0.3	10.7
	2017	<DL	<DL	<DL	1.5	0.4	4.4	2.5	1.1	1.7	2.3	0.5	0.7	0.8	0.5	0.8	17.2
	2018	<DL	<DL	<DL	2.1	<DL	4	4	1.6	2.1	3.6	1.3	1.1	1.7	<DL	2.3	23.8
GG1	2015	<DL	<DL	0.5	1.7	0.4	3.7	2.2	1.3	1.9	2.3	0.7	0.5	1	0.5	0.9	17.6
	2016	<DL	<DL	0.6	1.9	0.5	5.3	2.7	1.4	2.1	3	1.1	0.8	1.2	0.4	1.6	22.6
	2017	<DL	<DL	0.6	2.3	0.5	5.1	3	1.4	2.2	3.9	1.6	1.1	2	0.6	2.3	26.6
	2018	<DL	<DL	1	2.2		4.8	5.4	1.9	2.1	4.6	1.9	1.3	2	<DL	2.3	29.5
GG2	2015	<DL	0.3	0.7	3.4	0.8	10	5.3	3.1	4.7	5.7	1.6	1.4	2.3	0.8	2.8	42.9
	2016	<DL	<DL	<DL	0.6	0.2	2.3	1.6	1.6	2.4	4.1	1.8	2.8	2	0.5	2.8	22.7
	2017	<DL	<DL	0.8	1.9	0.5	5.7	3.5	1.6	2.1	3.9	1.5	1.1	1.5	0.4	1	25.5
	2018	<DL	<DL	<DL	1.8	<DL	3.5	3.1	1.5	1.7	4	1.5	1.1	2.3	<DL	2.8	23.3
YS1	2015	<DL	<DL	<DL	0.2	0.1	<DL	0.2	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	0.5
	2016	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	0.0
	2017	<DL	<DL	<DL	0.6	0.2	1.4	0.8	0.4	0.6	0.7	<DL	<DL	<DL	<DL	0.3	5.0
	2018	<DL	<DL	<DL	0.9	<DL	0.7	0.8	<DL	<DL	<DL	<DL	<DL	<DL	<DL	0.4	2.8
YS2	2015	<DL	<DL	<DL	0.3	0.1	0.7	0.4	<DL	0.5	<DL	<DL	<DL	0.3	<DL	0.2	2.5
	2016	<DL	<DL	<DL	<DL	<DL	0.8	0.4	<DL	<DL	<DL	<DL	<DL	<DL	<DL	0.2	1.4
	2017	<DL	<DL	<DL	<DL	<DL	0.7	0.4	<DL	<DL	<DL	<DL	<DL	<DL	<DL	0.2	1.3
	2018	<DL	<DL	<DL	0.8	<DL	0.8	0.9	<DL	<DL	0.6	<DL	<DL	0.3	<DL	0.4	3.8

[a] < Detection limit

Appendix 2. Individual SOs concentration in sediment from sampling sites.

Sampling		SOs concentrations (ng g^{-1} dm)										
Location	Year	SD1	SD2	SD3	SD4	ST1	ST2	ST3	ST4	ST5	ST6	Total
LS1	2010	0.6	<DL	3.1	<DL	7.5	<DL	0.3	1.4	0.4	0.6	13.4
	2012	<DL	<DL	10.9	<DL	3.8	<DL	<DL	<DL	<DL	<DL	14.8
	2014	<DL	<DL	5.7	<DL	4.0	<DL	0.3	1.5	0.4	<DL	11.8
	2017	<DL	<DL	<DL	<DL	1.0	<DL	<DL	<DL	<DL	<DL	1
	2018	<DL	<DL	3.8	<DL	<DL	<DL	<DL	<DL	<DL	<DL	3.8
LS2	2010	<DL	<DL	<DL	<DL	3.0	<DL	<DL	0.6	<DL	<DL	3.6
	2011	<DL	<DL	11.9	<DL	8.2	0.7	1.3	0.9	0.8	<DL	23.7
	2012	<DL	<DL	9.3	<DL	5.0	<DL	0.3	<DL	0.4	<DL	15
	2013	<DL	<DL	15.9	<DL	3.8	<DL	<DL	1.2	0.4	<DL	21.3
	2014	1.2	<DL	48.0	<DL	5.9	<DL	0.4	1.8	0.5	1.2	57.9
	2015	0.3	<DL	1.2	<DL	1.0	<DL	<DL	<DL	<DL	0.3	2.5
	2016	5.9	5.5	34.0	1.8	4.2	5.8	6.3	8.9	7.4	5.9	79.9
	2017	<DL	<DL	2.6	<DL	1.7	<DL	<DL	<DL	<DL	<DL	4.3
	2018	<DL	<DL	<DL	<DL	0.7	<DL	<DL	<DL	<DL	<DL	0.7
AS1	2010	<DL	<DL	1.2	<DL	2.9	<DL	<DL	<DL	<DL	<DL	4.1
	2011	0.6	<DL	2.4	<DL	3.0	<DL	<DL	<DL	<DL	0.6	6
	2012	<DL	<DL	7.0	<DL	3.3	<DL	<DL	<DL	<DL	<DL	10.3
	2013	<DL	<DL	6.4	<DL	3.0	<DL	<DL	0.8	<DL	<DL	10.2

	2014	<DL	<DL	6.2	0.3	3.7	<DL	<DL	1.1	<DL	<DL	11.2
	2015	<DL	<DL	<DL	<DL	0.6	<DL	<DL	<DL	<DL	<DL	0.6
	2016	<DL	<DL	16.3	<DL	<DL	<DL	<DL	<DL	<DL	<DL	16.3
	2017	<DL	<DL	1.0	<DL	1.4	<DL	0.7	0.6	0.4	<DL	4.2
	2018	<DL	<DL	1.2	<DL	0.6	<DL	<DL	<DL	<DL	<DL	1.8
AS2	2010	<DL	<DL	1.0	<DL	2.5	<DL	<DL	<DL	<DL	<DL	3.5
	2011	0.5	<DL	4.9	<DL	4.0	<DL	<DL	0.8	<DL	0.5	10.2
	2012	<DL	<DL	6.7	<DL	3.6	<DL	0.4	1.4	0.4	<DL	12.4
	2013	<DL	<DL	30.0	<DL	3.1	<DL	<DL	1.1	<DL	<DL	34.3
	2014	<DL	<DL	15.3	2.2	4.8	<DL	0.9	3.3	0.8	<DL	27.3
	2015	0.4	<DL	1.3	<DL	1.2	<DL	<DL	<DL	<DL	0.4	3
	2016	0.8	4.7	8.3	7.0	4.7	<DL	0.4	<DL	1.1	0.8	27.1
	2017	<DL	<DL	1.4	0.4	1.4	<DL	<DL	<DL	<DL	<DL	3.2
	2018	0.5	<DL	6.0	0.7	2.0	0.8	0.3	1.3	<DL	0.5	11.6
SG1	2010	0.6	<DL	<DL	<DL	2.7	<DL	<DL	<DL	<DL	0.6	3.3
	2011	<DL	<DL	7.2	<DL	3.0	<DL	<DL	<DL	<DL	<DL	10.2
	2012	<DL	<DL	11.0	0.4	4.7	<DL	1.0	3.4	0.8	<DL	21.1
	2013	<DL	<DL	6.2	<DL	3.0	<DL	<DL	1.1	<DL	<DL	10.3
	2014	<DL	<DL	7.2	<DL	3.9	<DL	<DL	0.8	<DL	<DL	12
	2015	0.4	<DL	<DL	<DL	1.0	<DL	<DL	<DL	<DL	0.4	1.4
	2016	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	0

	2017	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	0
	2018	<DL	<DL	3.6	<DL	0.7	<DL	<DL	<DL	<DL	<DL	4.2
SG2	2010	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	0
	2011	<DL	<DL	3.2	<DL	2.6	<DL	<DL	<DL	<DL	<DL	5.8
	2012	1.0	<DL	17.6	<DL	4.3	<DL	0.4	1.6	0.5	1.0	25.3
	2013	<DL	<DL	1.4	<DL	0.8	<DL	<DL	<DL	<DL	<DL	2.2
	2014	1.1	<DL	10.6	0.3	4.3	<DL	0.4	1.7	0.5	1.1	18.8
	2015	0.5	<DL	1.9	0.3	1.0	<DL	<DL	<DL	<DL	0.5	3.7
	2016	<DL	<DL	34.2	<DL	<DL	<DL	<DL	<DL	<DL	<DL	34.2
	2017	<DL	<DL	8.5	<DL	8.0	<DL	<DL	<DL	<DL	<DL	16.5
	2018	<DL	<DL	4.5	<DL	0.6	<DL	<DL	<DL	<DL	<DL	5.1
GG1	2010	2.1	<DL	4.4	<DL	9.8	<DL	0.4	1.1	1.2	2.1	19
	2011	0.4	<DL	5.2	<DL	6.7	<DL	0.7	<DL	1.7	0.4	14.8
	2012	0.4	<DL	36.9	<DL	3.7	<DL	0.4	1.8	1.4	0.4	44.4
	2013	<DL	<DL	5.2	<DL	1.4	<DL	<DL	<DL	<DL	<DL	6.6
	2014	0.9	<DL	30.0	0.8	4.1	<DL	<DL	1.1	0.4	0.9	37.2
	2015	0.5	<DL	1.4	0.5	1.3	<DL	0.6	<DL	<DL	0.5	4.3
	2016	<DL	<DL	<DL	<DL	0.5	<DL	<DL	<DL	<DL	<DL	0.5
	2017	<DL	<DL	<DL	<DL	1.2	<DL	<DL	<DL	<DL	<DL	1.2
	2018	<DL	<DL	1.7	<DL	0.7	<DL	<DL	<DL	<DL	<DL	2.4
GG2	2010	<DL	<DL	1.7	<DL	3.5	<DL	0.5	0.7	0.8	<DL	7.3

	2011	<DL	<DL	5.0	0.3	2.9	<DL	<DL	<DL	<DL	<DL	8.1
	2012	<DL	<DL	30.1	<DL	4.6	<DL	0.5	2.7	0.6	<DL	38.6
	2013	1.8	<DL	18.6	0.3	6.9	<DL	0.6	2.5	0.6	1.8	31.3
	2014	1.1	<DL	20.8	0.4	5.1	<DL	3.8	1.6	0.6	1.1	33.5
	2015	0.5	<DL	1.6	<DL	1.9	<DL	<DL	<DL	<DL	0.5	4
	2016	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	0
	2017	<DL	<DL	<DL	<DL	1.4	<DL	<DL	<DL	<DL	<DL	1.4
	2018	<DL	<DL	2.7	<DL	<DL	<DL	<DL	<DL	<DL	<DL	2.7
YS1	2010	<DL	<DL	7.5	<DL	7.5	<DL	0.8	0.8	0.4	<DL	16.9
	2011	<DL	<DL	3.0	<DL	2.4	<DL	<DL	<DL	<DL	<DL	5.4
	2012	<DL	<DL	6.1	<DL	4.5	<DL	0.4	1.4	0.3	<DL	12.8
	2013	<DL	<DL	6.6	<DL	4.7	<DL	0.4	1.2	<DL	<DL	12.9
	2014	0.4	<DL	11.7	0.6	4.6	1.5	0.9	3.1	0.7	0.4	23.5
	2015	0.6	<DL	2.2	<DL	3.6	<DL	<DL	<DL	<DL	0.6	6.4
	2016	<DL	<DL	15.9	<DL	<DL	<DL	<DL	<DL	<DL	<DL	15.9
	2017	0.6	<DL	9.3	<DL	0.9	<DL	<DL	<DL	<DL	0.6	5.8
	2018	0.6	<DL	9.3	<DL	0.9	<DL	<DL	<DL	<DL	0.6	6.9
YS2	2010	<DL	<DL	3.7	<DL	3.8	<DL	<DL	<DL	<DL	<DL	7.5
	2011	<DL	<DL	2.4	<DL	1.6	<DL	<DL	<DL	<DL	<DL	4
	2012	6.3	<DL	8.2	0.3	<DL	<DL	0.6	2.1	1.7	6.3	19.3
	2013	0.5	<DL	10.3	0.3	5.1	<DL	0.4	1.5	<DL	0.5	18

2014	0.8	<DL	92.3	0.5	4.4	<DL	0.3	1.1	<DL	0.8	99.4
2015	<DL	<DL	1.4	<DL	1.1	<DL	<DL	<DL	<DL	<DL	2.5
2016	<DL	<DL	<DL	<DL	<DL	<DL	<DL	0.5	<DL	<DL	0.5
2017	<DL	<DL	<DL	<DL	1.4	<DL	<DL	<DL	<DL	<DL	1.4
2018	<DL	<DL	3.9	<DL	0.6	0.6	0.9	0.6	0.4	<DL	4.4

[a] < Detection limit

Appendix 3. Individual NPs concentration in sediment from sampling sites.

Sampling		NPs concentrations (ng g^{-1} dm)			
Location	Year	NPs	NP1EOs	NP2EOs	Total
LS1	2017	2.1	0.7	1.0	3.8
	2018	1.6	<DL	<DL	1.6
LS2	2015	1.6	<DL	0.8	2.4
	2016	21.0	2.7	4.4	28.1
	2017	23.8	1.3	5.0	30.1
	2018	<DL	<DL	<DL	0.0
AS1	2015	<DL	<DL	0.9	0.9
	2016	<DL	<DL	<DL	0.0
	2017	11.2	1.4	2.7	15.3
	2018	<DL	<DL	<DL	0.0
AS2	2015	2.5	<DL	0.7	3.2
	2016	12.2	1.3	1.9	15.4
	2017	2.2	0.6	1.9	4.7
	2018	1.2	<DL	<DL	1.2
SG1	2015	0.7	<DL	0.7	1.4
	2016	<DL	0.5	0.9	1.4
	2017	4.9	0.9	1.0	6.8
	2018	<DL	<DL	<DL	0.0

SG2	2015	3.2	<DL	0.9	4.1
	2016	3.2	<DL	1.4	4.6
	2017	4.8	0.7	2.0	7.5
	2018	<DL	<DL	<DL	0.0
GG1	2015	4.3	<DL	1.1	5.4
	2016	37.1	3.4	3.6	44.1
	2017	19.2	4.3	5.4	28.9
	2018	14.9	3.1	<DL	18.0
GG2	2015	5.2	<DL	1.0	6.2
	2016	3.7	0.7	1.1	5.5
	2017	54.8	2.1	3.5	60.4
	2018	<DL	<DL	1.4	1.4
YS1	2015	<DL	<DL	1.3	1.3
	2016	2.3	0.6	0.8	3.7
	2017	1.7	<DL	1.2	2.9
	2018	<DL	<DL	<DL	0.0
YS2	2015	<DL	<DL	1.2	1.2
	2016	4.6	0.9	1.1	6.6
	2017	3.1	1.7	1.8	6.6
	2018	<DL	<DL	<DL	0.0

[a] < Detection limit

Appendix 4. Individual HMs concentration in sediment from sampling sites.

Sampling		HMs concentrations (mg kg^{-1} dm)							
Location	Year	AS	Cd	Cr	Cu	Hg	Ni	Pb (µg kg^{-1} dm)	Zn
LS1	2010	7.91	0.06	59.6	13.22	11.14	22	21.1	60.5
	2012	6.8	0.12	24	17	7.25	9	27	62
	2014	5.75	0.27	15.8	15.8	6.3	11.9	31.7	100
	2017	2.27	0.17	78.47	27.6	4.64	24.4	25.6	68.3
	2018	0.76	0.13	33.32	14.4	8.49	12.2	29.3	62.1
LS2	2010	4.02	0.07	77	12.88	15.39	29	26	55.8
	2011	3	0.1	70.4	12.6	13.8	25.9	23.1	56.3
	2012	4.29	0.15	29	10.4	4.02	19	27	65.5
	2013	4.06	0.15	46	11.17	4.44	27	26	54.2
	2014	7.88	0.26	64.1	9.98	6.84	36.9	24.3	48.8
	2015	1.99	0.11	54.2	10.1	8.55	15.9	18.0	54.1
	2016	2.45	0.15	74.48	9.4	22.16	23.5	22.8	48.7
	2017	2.73	0.14	73.6	9.3	17.84	24.2	20.5	51.5
	2018	2.67	0.2	87.73	9.6	26.35	28.6	24.2	46.4
AS1	2010	11.04	0.08	137	35	3.96	68	12	92
	2011	3.98	0	68.9	7.4	12.7	30.1	21.4	42.7
	2012	14.3	0.21	122	27	3.05	62	13	90
	2013	5.44	0.13	34.7	14.9	3.74	22.8	25.7	71.3

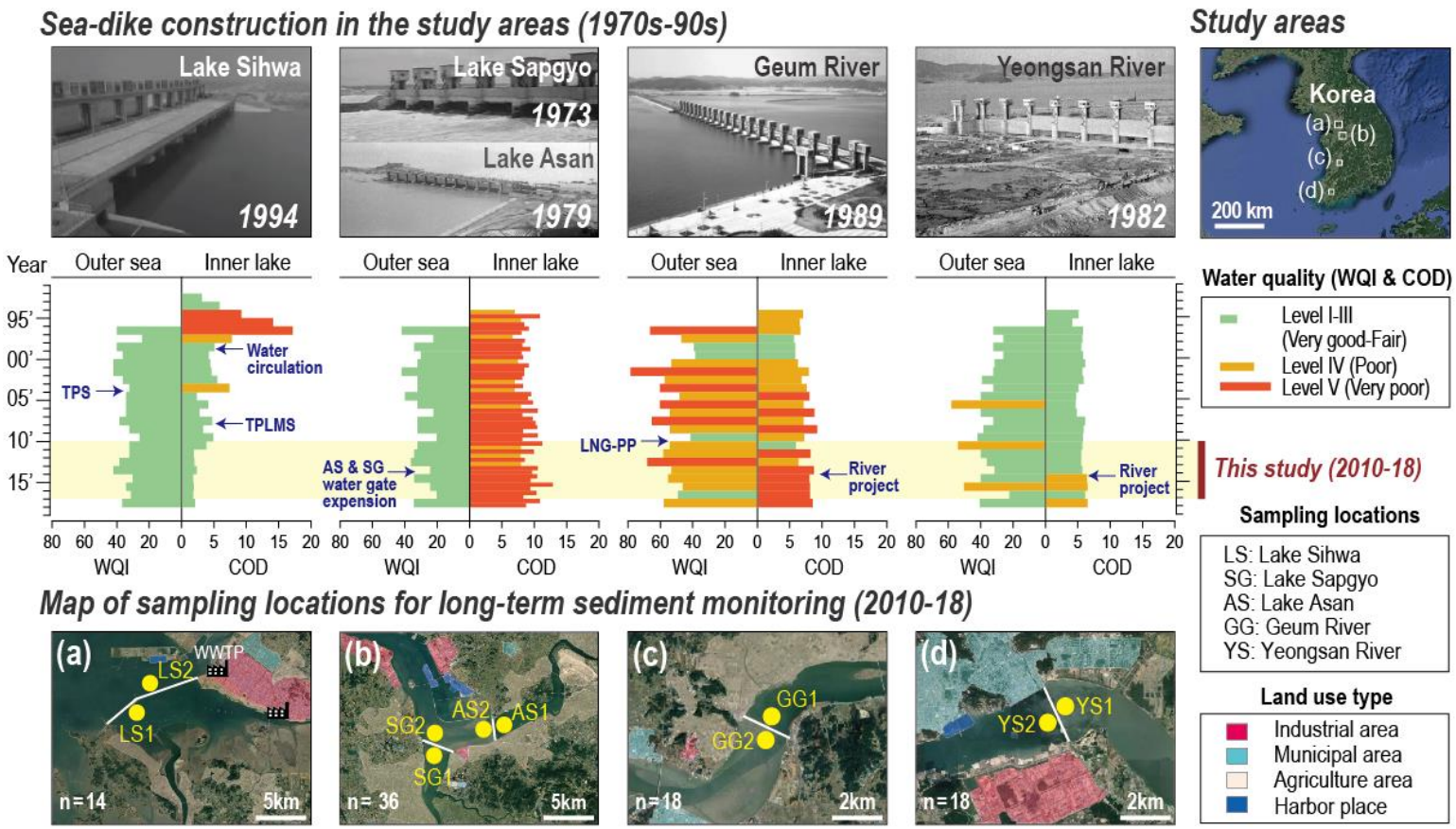
	2014	5.26	0.1	29.7	8.9	3.17	11.9	18.8	39.6
	2015	1.4	0.08	18.11	5.2	1.02	6.7	26.7	6.7
	2016	2.01	0.09	31.89	6.8	1.63	12.3	19.3	40.0
	2017	3.24	0.15	57.98	14.5	4.21	24.7	27.2	97.4
	2018	1.78	0.05	27.96	6.4	1.41	10.2	23.9	41.5
AS2	2010	4.47	0.07	7.8	13.7	4.25	3.9	69.6	87.3
	2011	3.66	0.1	79	9.6	17.1	38	31	48.9
	2012	4.8	0.29	22	46	6.23	11	13	63
	2013	6.1	0.18	47	9.9	5.7	30	13	48.1
	2014	9.29	0.26	85	9.72	13.06	36	21	47.7
	2015	2.57	0.17	58.62	15.4	15.97	21.4	21.4	21.4
	2016	1.35	0.19	66.86	15.4	18.66	26.1	23.9	59.4
	2017	2.84	0.12	66.11	10.1	18.55	24.4	20.4	49.4
	2018	3.16	0.15	65.47	13.2	17.49	25.2	26.7	58.7
SG1	2010	3.9	0.05	64.4	9	10.86	26.7	15.8	44.7
	2011	3.78	0	21.2	3.5	3.5	8.8	23	27.4
	2012	3.34	0.11	52.9	8.97	7.78	20.6	14.7	54.3
	2013	3.48	0.09	61.8	9.86	4.14	26.5	18.6	51.7
	2014	6.4	0.14	65.3	7.26	8.56	27.7	15.8	41.4
	2015	2.62	0.08	67.57	7.7	15.04	21.8	17.5	44.4
	2016	3.71	0.11	80.21	7.0	15.06	27.6	21.5	41.9

	2017	1.98	0.09	66.73	7.5	7.62	17.6	16.9	45.8
	2018	1.2	0.03	12.52	2.3	1.05	4.8	17.4	12.0
SG2	2010	6.55	0.06	71.3	9.66	11.1	30.7	25.7	47.8
	2011	3.69	0	72.3	10.8	10.9	29.7	26.7	47.5
	2012	8.22	0.17	75.2	9.08	18.48	36.6	23.8	47
	2013	5.48	0.12	53.4	8.08	5.29	22.3	25.2	48.6
	2014	7.36	0.32	48	12.48	7.26	26	19	46.1
	2015	4.44	0.15	101.93	7.6	24	35.9	32.2	44.1
	2016	2.79	0.15	69.98	20.7	23.64	25.4	21.8	84.8
	2017	2.41	0.16	65.1	10.4	16.47	23.2	20.8	48.0
	2018	3.59	0.15	85.26	7.8	24.78	31.5	24.5	43.2
GG1	2010	6.24	0.11	91.3	9.63	45.33	55.8	43.3	47.2
	2011	4.78	0.1	101	10	25.1	45	47	49.4
	2012	5.69	0.15	87	10.05	35.58	40	35	47.4
	2013	6.41	0.26	97.3	9.71	11.7	44.6	42	47.7
	2014	10.82	0.28	89.2	9.03	13.71	40.2	33.3	44.5
	2015	5.15	0.25	111.76	8.3	52.58	43.5	36.3	42.3
	2016	4.16	0.21	96.27	8.9	49.72	39.5	29.3	42.4
	2017	3.65	0.19	87.96	7.9	34.92	33.1	28.4	43.1
	2018	4.96	0.27	107.07	8.5	54.18	43.3	34.1	42.5
GG2	2010	3.98	0.07	76	9.45	27.37	34	34	47.6

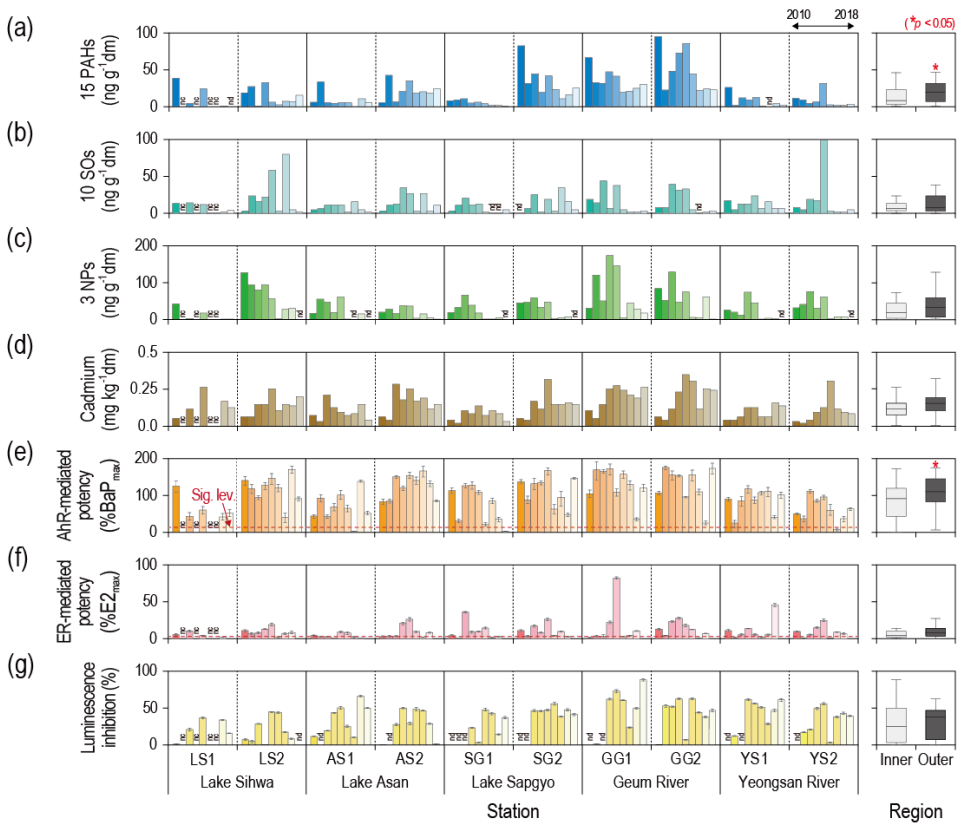
	2011	5.93	0	96.1	10.4	13.1	43.1	25.5	52.2
	2012	2.61	0.12	51.5	10	29.82	34	22.3	46.9
	2013	8.13	0.24	81	9.46	14.16	42	32	47.6
	2014	8.65	0.35	78	9.77	12.55	38	26	47.8
	2015	4.67	0.31	103.31	8.3	39.11	38.9	36.1	45.3
	2016	3.17	0.12	78.15	11.3	17.96	26.7	26.7	44.5
	2017	4.25	0.26	98.49	7.8	40.51	37.7	31.4	42.9
	2018	3.19	0.25	85.21	8.8	33.84	33.3	27.8	44.7
YS1	2010	4.15	0.04	64.4	6.28	6.54	29.7	25.7	44
	2011	3.55	0	77	6.4	6.9	35	24	44.1
	2012	2.45	0.07	39	28.33	7.02	20	16	52.2
	2013	6.65	0.13	76	8.39	4.8	32	20	43.4
	2014	6.07	0.13	78.8	6.61	4.44	33.6	25.7	43.2
	2015	2.56	0.07	50.56	5.8	6.23	14.8	23.6	38.9
	2016	2.95	0.07	75.07	6.1	7.55	20.4	20.5	38.4
	2017	3.59	0.16	57.16	7.5	12.2	20.2	25.9	44.6
	2018	4.31	0.14	87.34	6.9	11.29	29.7	27.4	42.2
YS2	2010	5.9	0.03	27	6.71	5.28	11	21	40.8
	2011	2.48	0	28.4	6.2	4.4	11.8	20.6	39.8
	2012	2.56	0.05	64.4	6.52	6.68	25.7	15.8	40.3
	2013	4.39	0.1	49.5	6.17	4.89	15.5	12.6	40.3

2014	6.11	0.13	71.1	7.7	4.03	28.9	14.9	42.5
2015	2.44	0.31	56.82	12.6	15.16	21.2	36.8	58.2
2016	4.68	0.12	104.39	6.2	9.9	35.9	28.2	39.5
2017	2.01	0.1	56.09	7.9	5.21	14.1	25.0	38.7
2018	3.27	0.09	81.64	6.5	7.32	23.7	25.2	40.0

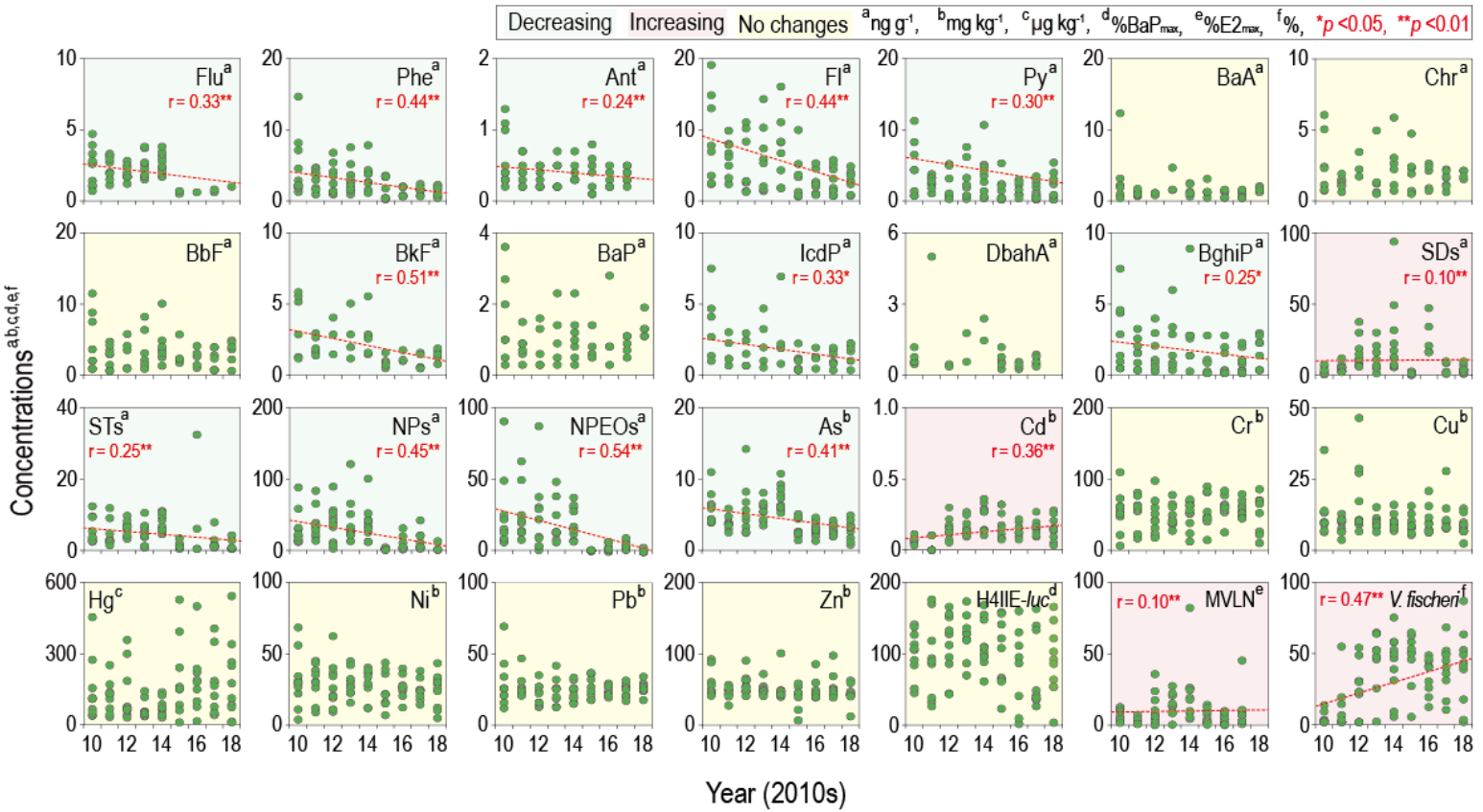
[a] < Detection limit



Appendix 5. Backgrounds of study area.



Appendix 6. Spatio-temporal distribution of PTSs and long term changes of potential toxicity in the sediments.



Appendix 7. Temporal trends of individual PTSs and potential toxicity in the sediments.

Abstract

우리나라 서해 연안은 지난 수십 년 동안 도시화 및 공업화가 급속히 진행되었고, 이로 인해 오염물질이 해양환경으로 유입되고 있다. 특히 서해 연안은 반 폐쇄성 해역이라는 지형적인 특성으로 인해 해수 교환이 상대적으로 느려 연안 지역에 위치한 산업단지로부터 배출되거나 대기를 통해 유입된 오염물질이 연안 퇴적물 내에 축적되는 경향을 보인다. 본 연구에서는 서해 연안 및 주요 하구역 퇴적물의 유기화합물의 분포 특성과 잠재적 생물 영향을 평가하였다. 2010년부터 2018년 까지 매년 시화호, 아산호, 삽교호, 금강 하구, 영산강 하구의 10개 정점에서 방조제를 중심으로 내, 외측으로 나누어서 표층 퇴적물을 채취하였다. 퇴적물을 유기 용매로 추출한 후 추출액을 극성 별로 분액 하여 가스크로마토그래피-질량분석기를 이용해 잔류성오염물질의 농도를 분석하였다. 15종의 다환방향족탄화수소, 10종의 스티렌올리고머와 3종의 노닐페놀을 정량 분석하였다. 유도결합플라즈마-질량분석기를 이용하여 8종의 중금속을 분석하였다. 또한 유전자 재조합 세포주인 H4IIE-*luc*과 MVLN을 이용하여 다이옥신류 활성 및 에스트로겐류 활성을 평가하였고, *Vibrio fischeri* 발광박테리아를 이용하여 퇴적물 내 잠재 독성 정도를 평가하였다.

서해 연안 퇴적물 내 다환방향족탄화수소 농도는 0.0 - 93.5 ng g^{-1} dry mass (dm)였고, 스티렌올리고머 농도는 0.0 - 23.2 ng g^{-1} dm 이었으며, 노닐페놀농도는 0 - 68.3 ng g^{-1} dm 이었다. 중금속 농도의 경우 해양환경 주의 기준과 서해 연안 퇴적물내 농도 비율을 통한 위험도 지수 (Hazard quotients)를 이용하여 오염 정도를 평가하였다. 모든 중금속의 위험도 지수를 합한 결과 0 - 6 사이 분포를 나타냈다. 분석 결과 서해 연안 퇴적물 내 잔류 오염 물질의 농도는 우리나라 연안 및 다른 나라에 비해 상대적으로 낮은 수준이었다.

잔류 오염물질의 개별 화합 물질 농도 비율을 통한 오염원 추적 결과 다환방향족탄화수소는 발열에 의한 생성이 대부분이었고, 특히 2015년 이후부터 자동차 배출가스로부터의 오염이 증가하는 것으로 나타났다. 스티렌올리고머와 노닐페놀의 분석결과 2010년도 이후 서해 연안 퇴적물내 새로운 유입이 서서히 감소하는 것으로 나타났다. 노닐페놀 농도의 감소는 한국 정부의 효과적인 노닐페놀 규제에 의한 것으로 사료된다.

다이옥신류 활성 평가 결과 모든 시료에서 높은 농도의 활성을 보였고, 에스트로겐류 활성 평가 결과 2015년 이후 감소하는 경향성을 보였다. 발광박테리아 활성 평가 결과 2010년부터 2013년까지 증가 후 비슷한 범위의 발광저해율을 유지하였다. 서해 연안 퇴적물내 잔류 오염물질의 농도 분포와 생물 영향 평가 결과를 비교하였을 때 다환방향족탄화수소 농도와 다이옥신류 활성 ($r = 0.53$, $p < 0.01$) 노닐페놀 농도와 에스트로겐류 활성 ($r = 0.31$, $p < 0.01$), 카드뮴 농도와 발광박테리아 발광저해율 ($r = 0.47$, $p < 0.01$)에서 각각 유의한 상관관계를 보였다. 생물 영향 기여도 평가 결과 서해 연안 퇴적물 내 다환방향족탄화수소와 스티렌올리고머의 농도가 총 다이옥신류 활성의 약 0.1%를 설명하였고, 노닐페놀의 농도는 에스트로겐류 활성을 설명하지 못했다. 이러한 결과는 본 연구에서 분석한 다환방향족탄화수소, 스티렌올리고머, 노닐페놀 이외의 다른 화합물들이 서해 연안 퇴적물에 존재하고 있으며, 잠재적인 생물 영향을 미칠 수 있음을 의미한다고 볼 수 있다. 따라서 향후 추가적인 화합물에 대한 장기모니터링 및 지속적인 연구가 필요할 것으로 사료된다.

주요어: 다환방향족탄화수소, 노닐페놀, 스티렌올리고머, 중금속, 생물 영향 평가, 퇴적물

학번: 2017-20790